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INDUSTRIAL WASTE SURVEY REPORT. GREAT LAKES STEEL CORPORATION

F. W. Kittrell, et al

Sanitary Engineering Center
Cincinnati, Ohio

1955

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INDUSTRIAL WASTE SURVEY REPORT

GREAT LAKES STEEL CORPORATION

March 28 to May 25, 1955

By

F. W. Kittrell and G. N. McDermott

Prepared for the

INTERNATIONAL JOINT COMMISSION

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TABLE OF CONTENTS

	Page
SUMMARY	1
GENERAL INFORMATION	
1. Organization of Project	7
2. Dates	7
3. Objectives	7
4. Personnel Participating	8
5. Location of Plants	8
6. Raw Materials	9
7. Production	9
8. Operations	10
9. Water Supply	10
10. Industrial Sewers	10
11. Sanitary Sewage	10
DISCUSSION OF PROCESS AND WASTE SOURCES	12
A. BLAST FURNACE DIVISION	13
12. Coking	13
13. Coke By-Products	13
14. Ammonia Liquor and Tar Recovery	14
15. Dephenolization of Ammonia Liquor	14
16. Ammonia Still	16
17. Naphthalene Recovery	17
18. Light Oil Recovery	18
19. Light Oil Refining	18
20. Ore Reduction	19
21. Blast Furnace Gas Cleaning	19
22. Wash Water Disposal	20
23. Recovery of Dust	21
B. ECORSE PLANT	22
24. Bessemer Converters	22
25. Open Hearth Furnaces	22
26. Rolling	23
27. Pickling	23
28. Oil Recovery	26
SURVEY PROCEDURES	27
29. Sample Collection and Preservation	29
30. Flow Measurements	29
31. Laboratory Procedures	32
	34

TABLE OF CONTENTS

		Page
QUANTITY AND CHARACTER OF WASTES		35
32.	Presentation of Data	35
33.	Discussion of Data	36
CONTEMPLATED CHANGES IN PRODUCTION AND CONTROL OF WASTES		42
34.	Increased Production	42
35.	Oil Recovery	43
36.	Waste Pickle Liquor Disposal	43
37.	Improved Operation of Ammonia Stills	43
38.	Improvement of Carbolate Quality	44
39.	Contaminated Water System Changes	44
40.	Waste Sampling Program	44

APPENDICES

Appendix A	Tabulation of Data	45
Appendix B	Analyses Performed, Significance and Method	50
Appendix C	Relationship Between Contaminants in Coke Quenching Water and in Blast Furnace Gas Wash Water	56
Appendix D	Process Flow Diagrams	84

SUMMARY

This report describes and presents the findings of studies of liquid wastes at two Great Lakes Steel Corporation plants. These plants are the Blast Furnace Division (coke plant and blast furnace) on Zug Island in Detroit, and the Ecorse Plant (converters and rolling mills) in Ecorse, Michigan.

The purposes of the studies were to determine the effectiveness of certain water pollution control measures placed in operation in recent years and the possible need for additional control facilities. Measures at the Zug Island plant included: installation of a benzol extraction plant for removing phenols from ammonia liquor; quenching of coke with contaminated coke plant wastes; and alteration of the blast furnace gas wash water Thickeners to obtain more efficient settling. That at the Ecorse plant was installation of an oil skimming basin for removal of oil from one effluent of the rolling mill.

The volume and characteristics of selected effluents from the Ecorse Mill were determined in order to judge the need for control measures on these particular effluents.

In the study of the coke plant waste disposal methods at the Blast Furnace Division a special investigation was made of the carryover of phenols and other contaminants, in the wastes used for coke quenching, to the blast furnace. In the furnace they volatilize and subsequently condense with the blast furnace gas wash water waste. Quench water containing a range of concentrations of the wastes was used for coke quenching and concentrations of certain pollutional materials in the related blast furnace gas wash water were determined.

The results showed a direct relationship between concentration of phenols in the coke quenching water and the concentration of phenols in the blast furnace gas wash water. No similar correlation in carryover of ammonia or cyanide was evident. The following table presents estimates of phenol loads to the river that might result from various methods of operating the phenol disposal system. The estimates are based on results of the special study.

ESTIMATED PHENOL LOADS TO RIVER WITH DIFFERENT QUENCHING AND DEPHENOLIZATION ARRANGEMENTS

Quench Water Supply	Wastes to River	Phenols to River in Blast Furnace Gas Wash Water and Coke Plant Wastes
Fresh Water	Blast furnace gas wash water, dephenolized ammonia liquor, ammonia concentrator wastes, and other coke plant wastes	368
Total coke plant wastes, with efficient dephenolization of ammonia liquor	Blast furnace gas wash water	48
Total coke plant wastes without dephenolization of ammonia liquor	Blast furnace gas wash water	113

The company planned to dispose of all contaminated coke plant wastes by evaporation in coke quenching. With this plan in effect the wastes discharged to the river directly from the by-product coking plant would consist of cooling water used in indirect coolers. The carryover of contaminants in the quench water to the blast furnace gas wash water would be the only source of waste materials discharged to the river from the coke plant. At the time of this study some of the necessary piping connections, equalizing tanks, and corrosion

resistant valves for consuming all the contaminated coke plant wastes in coke quenching had not been installed. There was an appreciable amount of coke plant wastes overflowing directly to the Detroit River from the coke plant.

The significant waste from the blast furnace department is the blast furnace gas wash water. The wash water is treated by sedimentation in Dorr Thickeners. The volume of the waste, and net concentrations and quantities of certain materials in the treated gas wash water discharged to the river are tabulated below. These data are based on sampling and analysis of the Thickener effluent.

BLAST FURNACE GAS WASH WATER

	Net Concentration Avg. ppm	Net Quantity Avg. Per Day lbs.	Quantity Per Ton of Coke lbs.	Quantity Per Ton of Pig Iron lbs.
Phenols	0.44	54	0.011	0.012
Ammonia (N)	5.4	671	0.14	0.15
Cyanides (CN)	0.60	74	0.015	0.016
Suspended Solids	838	103,000	20.9	22.7
Settleable Solids	800	98,400	19.9	21.7
Flow, gallons		14,760,000	3000	3200

The 54 pounds per day of phenols is higher than the estimated 47 pounds per day for quenching with total coke plant wastes including efficiently dephenolized ammonia liquor, in the previous table. The estimated value was based on an assumed 95.5 per cent dephenolization of the ammonia liquor. Plant records showed an average of only 88.2 per cent phenol recovery during the period of Thickener effluent sampling.

The ammonia stills were being operated experimentally during the sampling period, and recoveries were erratic. Less ammonia than that shown in the table should be lost after normal efficient operation of the stills goes into effect.

Cyanides were low, and probably were typical of normal operation.

The solids data reported in the table are thought to represent normal operations. During the first week of the study part of the gas wash water wastes by-passed the Thickeners and solids data for the period were not considered normal. Treatment of the wastes in the Thickeners during the normal operation period accomplished 88 per cent reduction in suspended solids and 90 per cent reduction in settleable solids.

The wastes from the Ecorse plant consisting of cooling water, descaling water, and spent pickle liquor, are discharged through five outfall sewers, designated as effluents Nos. 1 through 5. An additional sewer, No. 3A, carrying spent pickle liquor, discharges to No.3 sewer as it enters Detroit River. These two sewers were sampled separately. The No.4 sewer contains a large portion of the oil bearing rolling mill wastes and discharges to an oil skimming basin. An estimated 14,540 pounds per day of oil are removed by the oil skimmer. Tests of the effluent indicated that 8310 pounds per day were contained in the separator effluent. This indicates the separator removes about 64 per cent of the oil in this waste.

The volume and characteristics of the effluent from the oil-skimming basin and effluents No. 1, 3, and 3A, are tabulated below. Effluents Nos. 2 and 5 were not measured or sampled during this survey. Sewer No. 5, which carries wastes from open hearth furnaces, was judged not to contain significant quantities of pollutants. An oil skimming basin is planned for outfall No.2 and no data prior to construction of the treatment facility was considered necessary.

EFFLUENT FROM ECORSE PLANT

Outlet Number	Flow gpd	Oil		Suspended Solids		Acidity As $CaCO_3$ Total Unneutralized	
		ppm	lbs/day	ppm	lbs/day	ppm	lbs/day
No. 1	6,730,000	1.6	90	17	960		
No. 3	54,000,000	-	-	32	14,600	125	56,300
No. 3A	249,000	-	-	53	111	72,500	150,700
No. 4	7,300,000	137	8,310	67	4,080	509	31,000

Progress in pollution abatement by the company includes improved disposal of sanitary sewage. The sewage is either discharged to municipal sewerage systems or is settled in septic tanks and disinfected with chlorine before discharge to the Detroit River.

Plans under way and contemplated by the company for additional water pollution control measures include:

(1) Installing necessary piping and regulating equipment for consumption of all coke plant wastes in coke quenching.

(2) Installing oil skimming basins on the No. 2 and No. 3 effluents from the Ecorse Plant.

(3) Increasing the freeboards of the Thickeners to prevent short circuiting of the blast furnace gas wash water from the surface of the first settling units directly to the effluent troughs.

(4) Reducing the size of the outlet port of the oil separator on No. 4 sewer at the Ecorse Plant from 10 by 12 feet to about 3 x 4 feet. Plant engineers believe that this would increase efficiency of oil recovery by reducing disturbances caused by wave action on the river.

(5) Changing from soluble to insoluble oil for cooling in the cold rolling mill, which should increase the efficiency of the oil separator and reduce oil loss to the river.

(6) Operating the waste pickle liquor pumps and equalizing tank to assure more nearly uniform discharge of acid to the river.

(7) Establishing a routine program for sampling and analysis of wastes.

GENERAL INFORMATION

1. Organization of Survey

Representatives of the Michigan Water Resources Commission, the Great Lakes Steel Corporation (Division of National Steel Corporation), and the Public Health Service met on March 21, 1955, to discuss plans for surveys of industrial wastes at the corporation's Blast Furnace Division Plant on Zug Island, and at their Ecorse Rolling Mill.

The Public Health Service furnished supervisory and technical personnel, laboratory equipment and supplies, and flow measuring devices, made flow measurements and chemical analyses, and prepared the report. Great Lakes Steel provided sampling personnel, physical structures necessary for flow measurements and sampling, and information on plant processes, raw materials, products and wastes. The Michigan Water Resources Commission arranged the preliminary contacts, assisted in planning, and acted in an advisory capacity during the field survey.

The project was part of the United States and Canadian International Joint Commission program to resurvey pollution of international waters in evaluating progress in water quality improvement since the 1947-1948 survey.

2. Dates

Wastes discharged to the Detroit River at the Blast Furnace Division Plant were sampled during May 1 to 6, 1955, and additional 24 hour composites were collected May 22-23 and 24-25.

Ecorse rolling mill wastes discharged to the Detroit River were surveyed during May 8 to 13, 1955.

A special in-plant study of phenol carryover into the blast furnace gas

wash water wastes from phenol bearing wastes used to quench coke was made at the Blast Furnace Division. Dates are given in the report on this work in the Appendix.

3. Objectives

The surveys were conducted for the following purposes:

a. To determine the quantities and characteristics of selected wastes discharged to the Detroit River by the Blast Furnace Division and Ecorse plants.

b. To measure the efficiency of blast furnace gas wash water waste solids removal by the Dorr Thickeners at the Blast Furnace Division plant.

c. To estimate the efficiency of oil removal by the oil separator on the cold mill sewer at the Ecorse plant.

d. To measure the effectiveness of phenol control measures, including dephenolization of ammonia liquor and evaporation of phenol bearing wastes by use in quenching coke, at the Blast Furnace Division coke plant.

4. Personnel Participating

Great Lakes Steel personnel who participated in the survey included:

D. E. McGuire, Vice President in Charge of Engineering
P. C. Vetter, Chief Engineer
Ernest Fuller, Research Engineer
Robert O'Hara, Chief Chemist, Ecorse Plant
W. H. Collison, Superintendent, Blast Furnace Division
James Beale, Secretary to the Superintendent, Blast Furnace Division
J. A. Greek, Asst. Supt., Coke Plant, Blast Furnace Division
Herbert Stiles, Chemist, Blast Furnace Division
Anderson, Engineer, Blast Furnace Division

MICHIGAN WATER RESOURCES COMMISSION
F. B. Frost, Sanitary Engineer

PUBLIC HEALTH SERVICE

Hayse H. Black, Sanitary Engineer Director
G. N. McDermott, Sanitary Engineer
F. W. Kittrell, Public Health Engineer
P. E. Langdon, Jr., Sanitary Engineer
R. C. Kroner, Chemist
C. N. Shadix, Chemist
C. R. Hirth, Chemist
F. J. Ludzack, Chemist

5. Location of Plants

The Blast Furnace Division plant is located on Zug Island and is bounded by the Detroit River, the River Rouge, property of Solvay Process Division, Allied Chemical & Dye Corporation, and the Del Ray Connecting Railway.

The Ecorse plant is located in Ecorse, Michigan and is bounded by the Detroit River, Nicholson Terminal & Dock Company property, Grasselli Chemical Company property, and the Michigan Central Railroad.

Although the plants are more than two miles apart they constitute, in effect, a single production unit. Molten pig iron from the Blast Furnece Division is transported by rail to the converters and rolling mills at the Ecorse plant.

6. Raw Materials

Raw materials used at the plants include:

a. Blast Furnace Division

Coal	6,200 tons per day

b. Ecorse Plant

Sulfuric Acid (60°Be')	150 tons per day
Mreasol (Lubrication)	3,870 pounds per day
Oil (Lubrication)	1,421 gallons per day
Oil (Cold Rolling)	2,174 gallons per day
Oil (Rust prevention)	1,025 gallons per day

7. Production

Materials produced at the Blast Furnace Division plant included:

Coke	4,800 tons per day
Pig Iron	4,400 tons per day

8. Operations

Operations at both plants were continuous, 24 hours per day, seven days per week.

9. Water Supply

a. Blast Furnace Division

Industrial process water is taken from the Detroit River through an intake channel and screen house. The intake is near the northeast corner of the plant, about 500 feet downstream from the mouth of the natural channel of Rouge River. Daily consumption averages 65 million gallons. Chlorination is the only treatment.

Thirty-eight thousand gallons of water per day from the Detroit municipal supply is used for sanitary purposes.

b. Ecorse Plant

Process water is taken from the Detroit River through a screen house. The intake is near the east corner of the plant, about 900 feet downstream from the No. 2 slip of the Nicholson Terminal Dock Company. Daily consumption averages about 100 million gallons. Chlorination is the only treatment.

A daily average of 1.1 million gallons is taken from the Detroit municipal supply for sanitary purposes.

10. Industrial Sewers

a. Blast Furnace Division

Major industrial sewers, with numbers assigned by the company, and

the plant areas served are listed below. The sewers are numbered consecutively starting with the one farthest upstream. All sewers are concrete, and discharge below the surface of Detroit River along the eastern boundary of the plant.

Sewer No.	Size	Areas Served
1	36"	Blast furnace gas wash water waste pump house by-pass, Furnaces "B" and "C".
2	48"	"B" and "C" Furnaces, Blower House No. 1, and Boiler House No. 1
3	36"	No. 1 Coke and By-Product Plant
4	30"	Dorr Thickeners, receiving blast furnace gas wash water waste from Furnaces "B", "C" and "D"
5	8"	"D" Furnace, Blower House No. 2, Boiler House No. 2, and No. 2 Coke and By-Products Plant

Sewer No. 4 only was sampled during this survey.

b. Ecorse Plant

Major industrial sewers, with numbers assigned by the company, and the plant areas served are listed below. They discharge to the Detroit River along the northeast boundary of the plant.

Sewer No.	Size	Areas Served
1	60"	No. 3 Slabbing Mill, including motor room. Wastes pass through a scale pit, which is equipped for oil removal also.
2	72"	No. 1 Open Hearth (12 furnaces), No. 1 Hot Strip Mill, Nos. 1 and 2 Merchant Mills, No. 1 Blooming Mill, and No. 1 Bar and Billet Mill.
3	84"	No. 2 Hot Strip Mill, No. 2 Blooming Mill and Pickling Room. A 12" acid resistant sewer (3A) carrying concentrated waste pickle liquor discharges into this sewer within a few feet of its mouth.
4	60"	Cold Mill. Wastes pass through an oil separator built into the bank of the river. Discharge is through an outlet port a few feet below the surface of the river.
5	60"	No. 2 Open Hearth (5 furnaces).

The sizes given are for the main sewers. All have enlarged outlet structures varying from 25 to 90 feet in length.

Sewers No. 1, 3, 3A, and 4 were sampled during the survey.

11. Sanitary Sewage

a. Blast Furnace Division

All sanitary sewage is settled in septic tanks and chlorinated before discharge to the Detroit River.

b. Ecorse Plant

Sewage from 90 per cent of the employees discharges to the Detroit municipal sewerage system. That from the remaining 10 per cent is settled in septic tanks and chlorinated before discharge to the Detroit River.

DISCUSSION OF PROCESS AND WASTE SOURCES

The two plants operate together to produce rolled steel products from iron ore. At the Blast Furnace Division coal is coked to yield coke and by-products. The coke and limestone are mixed with iron ore and scrap iron in three blast furnaces to produce molten pig iron. The molten pig iron is transported by rail in torpedo cars to the Ecorse Plant. Here the pig iron is converted to steel in open hearth furnaces, with a portion of the iron being blown first in Bessemer converters. The molten steel is teemed to produce solid ingots, which are rolled and otherwise processed to produce hot and cold rolled strip, sheet, structural, bar and other Merchant mill steel products. A major portion of the production is sheet steel used for automobile bodies. Soluble oil is used in the cold rolling process, and concentrated sulfuric acid is used for pickling in the hot strip process.

Figures 1, 2 and 3 in the Appendix show these processes diagramatically.

A. BLAST FURNACE DIVISION

12. Coking

Coal is coked in three batteries of vertical flue combination coke ovens. Two batteries of 146 ovens constitute the older No. 1 coke plant, and one battery of 70 ovens constitutes the new No. 2 coke plant. The two batteries of the No. 1 plant are designated as the East Battery and West Battery. This plant has a designed capacity of 4,400 tons of coal per day, and the No. 2 plant has a capacity of 1,800 tons per day for a total of 6,200 tons per day. The coke yield is 4,770 tons per day, or 77 per cent of the coal used.

During the seven days that samples were collected from the blast furnace gas wash water wastes coke production averaged 4,942 tons per day, rep-

resenting 6,420 tons of coal. Of this about 4,020 tons were handled by the No. 1 plant and 2,400 tons by the No. 2 plant. Only 3,278 tons of coke per day was needed for the blast furnaces during this period. The remaining capacity of the ovens was available for use in the new blast furnace that was under construction.

Coking times averaged 15 hours and 13 minutes at the No. 1 plant, and 16 hours at No. 2. Coking temperature was 2,600° F. (1,427°C) at both plants.

Coke is quenched with contaminated water from the coke by-products plants Fig. 1. Waste water containing phenols, ammonia, cyanides and thiocyanates from the by-products processes is collected in a contaminated water system and delivered to the three coke quenching stations serving the three batteries of ovens. The hot coke evaporates the contaminated water and most of the phenols and other contaminants but portions of the contaminants remain in the coke and accompany it to the blast furnaces.

13. Coke By-Products

The vapors and gas produced at both coke plants are processed for recovery of coke by-products. The equipment and methods of the old and new plants differ for the initial phases of this operation. In the latter phases of by-product recovery the gas and liquor of the two coke plants are combined for recovery operations.

14. Ammonia Liquor and Tar Recovery

At the old plant (No.1) the gases are first partially cooled and tar flushed out of gas collecting mains by liquor sprays and countercurrent contact with liquor in cooling towers. The liquor is cooled in indirect heat exchangers and recirculated through the primary and secondary cooling towers

and mains. Before recirculation it is passed through decanting tanks where tar is removed. The excess cooling and flushing liquor, amounting to about 20 gallons of weak ammonia liquor per ton of coal coked, is pumped to weak liquor storage. This weak liquor consists of condensed vapors from the gases, and is a water solution of the absorbed ammonia, phenols, and other coal derivatives.

Following the coolers the gases pass through tar precipitators and sulfur scrubbers to ammonia scrubbers. The ammonia scrubbers are three towers through which the gas flows in series. Fresh water is introduced through sprays into the top of one tower and flows countercurrent to the gases through the three scrubbers in turn. The scrubbers remove additional ammonia and phenols which have not been absorbed by the cooling and flushing liquor. The volume of liquor from the scrubbers is about 30 to 35 gallons per ton of coal coked. The liquor from the ammonia scrubbers is fed to an ammonia concentrator. Ammonia is stripped from the liquor by steam. The overhead vapors are condensed by an indirect condenser. This weak ammonia liquor, amounting to about 10 gallons per ton of coal coked, is combined with the weak ammonia liquor from the flushing and cooling process and goes to weak liquor storage. The steam stripping of the liquor removes most of the ammonia, but only an insignificant part of the phenols. The stripped ammonia scrubber liquor and condensed steam from the still were estimated by the company to contain the following:

Phenol	180 ppm
Free ammonia	50 ppm
Fixed ammonia	90 ppm

This corresponds to about 180 pounds of phenol per day. The cooling water used

in the overhead condenser joins the waste and the combined flow goes to the contaminated water system, from which it is used for coke quenching. It flows first to the east station of the No. 1 coke plant, and any excess goes to the west station.

At Plant No. 2 the conventional semi-direct system of gas cooling and ammonia recovery is employed. In this system the gases are initially cooled by recirculating condensed vapors from the gases (flushing liquor) through the gas collecting mains and a cooling tower in much the same manner as in Plant No. 1. Gas scrubbing with fresh water for ammonia absorption is omitted at this plant. The flushing liquor is passed through decanters where tar is removed, and the liquor is cooled and recirculated. The liquor is produced by the ovens at the rate of about 20 gallons per ton of coal coked. An equivalent volume is drawn continuously from the recirculating system as weak ammonia liquor and goes to weak liquor storage.

After initial cooling the gas passes through sulfur scrubbers to an ammonia absorber where ammonia is absorbed directly in sulfuric acid to produce ammonium sulfate. The gas then goes to a final cooler as described in a subsequent section.

15. Dephenolization of Ammonia Liquor

The weak ammonia liquor from the three sources is taken from storage to a benzol extraction dephenolizer. Any tar or light oil separating from the ammonia liquor in storage is drawn from the storage tanks and returned to appropriate streams in the process.

The 200,000 gallon per day dephenolization plant is designed to remove phenol compounds from weak ammonia liquor and recover the product in the form of sodium carbolate.

The ammonia liquor is pumped through a set of distributor pipes at the top of a scrubber. It flows downward through the wood grid packing in the scrubber countercurrent to an ascending flow of light oil (chiefly benzol), which is introduced through a distributor near the bottom. The light oil absorbs the phenol through the action of preferential solubility. The dephenolized ammonia liquor flows from the bottom of the scrubbers to the ammonia still. The phenolized light oil passes from the ammonia scrubber to a sulfur scrubber. In the sulfur scrubber the phenolized light oil is given a water wash. A 20 GPM stream of fresh water fed to the unit contacts the phenolized light oil and removes part of the hydrogen sulfide and other undesirable compounds. This contaminated water is conducted to the final cooler recirculation system. The phenols in the light oil are reacted with caustic soda in a two stage caustic washer to form sodium carbolate. When the caustic solution in the second stage of the contact reaches the desired carbolate concentration, it is discharged to the first stage and replaced with fresh caustic. In the first stage the caustic reacts with additional phenol and finally goes to the carbolate concentrator.

The dephenolized light oil is returned to the ammonia liquor scrubber and recirculated.

Oil and naphthalene and water are stripped from the sodium carbolate by steam stripping. The vapors from the stripper are returned to the gas main. The carbolate, concentrated to 50 per cent, is stored for sale.

16. Ammonia Still

The dephenolized weak liquor goes to a storage tank with 24 hours detention capacity, and from there to three ammonia stills. These stills have both

free and fixed legs, with lime applied in the fixed legs to liberate the fixed ammonia from its salts. The ammonia gas from the stills joins the coke oven gas from coke plant No. 2 ahead of the ammonia absorber at the sulfate plant.

The waste from the ammonia stills flows to a lime settling basin and thence to the contaminated water system for use in quenching coke. This end of the contaminated water system serves the quenching station at No. 2 plant first, with any excess going to the west quenching station of coke plant No. 1.

17. Naphthalene Recovery

The gas from coke plant No. 2 is cooled in the final cooler to condense water vapor and naphthalene. The gas continues to the light oil recovery plant.

The mixture of water and naphthalene flows to a skimming tank from which naphthalene is skimmed, treated with sulfate solution from the sulfate plant, and dried for sale. The water goes to the final cooler water pump basin, where a portion is recirculated to the final cooler and the excess overflows to the contaminated water system. Floor drains in this building also discharge to the contaminated water system.

18. Light Oil Recovery

Separate, but similar, plants are provided for recovery of light oil.

The gas from coke plant No.1 flows from the ammonia scrubbers directly to the No.1 light oil plant. That from coke plant No. 2 passes through the ammonia absorber and the final cooler, as described above, before going to the No. 2 light oil plant.

In both plants the gases are scrubbed with wash oil to remove light oil. The scrubbed gases from both plants join in the surplus coke oven gas main, are mixed with cleaned blast furnace gas and are piped to the Ecorse rolling

mill plant for use.

The benzolized (containing light oil) wash oil is preheated and then stripped of light oil with steam. The stripped wash oil is recirculated to the light oil scrubbers. The light oil and steam vapors are condensed, with the condensate flowing to a muck tank decanter and from there to the contaminated water system. The crude light oil from the two coke plants joins to go to a single light oil refining plant.

19. Light Oil Refining

A residue is separated from the crude light oil in a separating column. The residue is processed in a stripper, which also receives vapors from the tar boilers. The product is sold as carbolic oil, containing one per cent phenol.

The light oil is further refined in the benzol plant. It is washed with acid, caustic, ammonia and water, before going to a pure still residue removal unit. Here a pure still residue is removed and the light oil passes to a forerunnings unit. The forerunnings, consisting of carbon disulfide and other gases, flow to the plant gas main. Wastes, from the washing through the forerunnings processes, are siphoned by steam ejection to the lime settling basin, and thence discharged to the contaminated water system.

The forerunnings free light oil is further fractionated to yield benzol, xylol, toluol, solvent naphtha, heavy solvent, and a crude residue. There are said to be no liquid wastes from this operation.

20. Ore Reduction

The process of reducing iron ore to pig iron and the sources of wastes produced are shown in Fig. 2 of the Appendix.

Iron ore, limestone and coke from the two coke plants are charged to three

blast furnaces, designated as B, C and D by the company. The older A furnace was being replaced by a new and larger A furnace during the waste survey. B and C are standard furnaces, operating only slightly above atmospheric pressure. D is a pressure top furnace, operating under a pressure of several pounds per square inch.

In the furnace the high temperatures maintained by the combustion of the coke, augmented by the hot blast from the stoves furnishing air to the process, melt the three raw materials. The oxygen of the iron oxide ore combines with the carbon of the coke to form carbon monoxide. The molten iron is drawn from the furnace as pig iron and transported to the Ecorse plant for conversion to steel, and for rolling into various fabricated forms.

The impurities are retained in the slag formed by the limestone. The molten slag is run to a slag pit where it is cooled rapidly by water sprays to form granules of proper size for use as ballast.

During the plant waste survey the three furnaces produced an average of 4,546 tons of pig iron per day, of which D furnace produced 1,687 tons per day. The average coke use for the entire plant was 1,442 pounds per ton of pig iron produced, with D furnace averaging 1,496 pounds per ton.

21. Blast Furnace Gas Cleaning

The gas from the furnaces carries quantities of dust, consisting principally of coke, ore and limestone particles. This must be removed before the gas is suitable for use as fuel.

The gas first passes through a dust catcher, in which reduction in velocity and sudden change in direction permit separation of more than half of the dust. This dust is sintered and returned to the furnace.

The gas then goes to a washer in which it contacts sprays of water pre-

viously used to cool the furnace sidewalls. This removes an additional portion of the dust as a suspension in the blast furnace gas wash water waste. The wash water waste is withdrawn from the bottom of the washer.

From the washer the gas flows to the electrostatic precipitator. The dust is deposited on electrodes and washed from them by a thin film of flowing water. This is discharged as precipitator irrigation water. The flow of the gas to the precipitators is controlled by septum valves, on which some dust collects. These are washed clean by a small flow of water which is discharged as septum valve waste water.

A portion of the cleaned gas is returned to the furnace stoves, and the remainder is mixed with coke oven gas and carried to the Ecorse plant for use as fuel.

22. Wash Water Disposal

The waste water from the gas washers, the precipitators, and the septum valves flows together and is pumped to two Dorr Thickeners. The Thickeners were operating in parallel.

The Thickeners are circular two story settling tanks. The inflowing wash water waste discharges through revolving pipes at the surface of each tank. The discharge is directed from the center toward the periphery of the tank. At the peripheral wall the flow turns downward and returns to the center along the bottom of the top story. At the center it passes through an opening into the bottom story and again flows outward. At the wall it enters riser pipes equally spaced around the periphery of the tank. The riser pipes discharge into a peripheral trough that collects the waste water and carries it to the sewer.

Each of the two Thickeners has a volume of 675,000 gallons. This provides

a theoretical detention time of 2.2 hours for the wash water waste flow of 14.76 million gallons per day.

23. Recovery of Dust

The suspended material settles to the bottom of the Thickener as a sludge, which is pumped to vacuum filters. The relatively small volume of water filtered from the sludge normally is quite clear. It discharges to a small sewer paralleling the main Thickener effluent sewer.

The filter cake is combined with the dust from the dust catcher, sintered, and returned to the blast furnaces.

B. ECORSE PLANT

The processes at the Ecorse plant includes all operations necessary to convert pig iron to steel, and to roll and otherwise treat the steel to produce strips, sheets, bars and other structural forms. The major processes are diagrammed in Fig. 3, and are described below.

24. Bessemer Converters

The molten pig iron brought from the Blast Furnace Division to the Ecorse plant in ladle cars is poured into a hot metal mixer. This serves to store the metal in the molten state. From the mixer this still molten metal is transferred either directly to an open hearth furnace or first to a Bessemer converter and subsequently to an open hearth furnace. Only a portion of the total production is blown in the Bessemers, but the entire production is processed in open hearth furnaces.

In the Bessemer the molten pig iron is blown with air, which is introduced at the bottom. The heat of the molten metal and of oxidation reactions that take place provides the temperatures necessary to burn out, or oxidize,

carbon and other impurities. This converts the pig iron to semi-finished steel.

25. Open Hearth Furnaces

Either molten pig iron or semi-finished steel from the Bessemers is treated in the 17 open hearth furnaces. Here, also, impurities are eliminated to produce steel. There are two basic differences between the Bessemer and open hearth processes. In the Bessemer no heat is added beyond that already in the molten pig iron, and that caused by the oxidation reactions. Most of the oxygen used is from the oxygen in the air blast. In the open hearth furnaces heat is added, usually by gas burning in the furnaces above the molten metal. Much of the oxygen used is from materials added to the molten metal, such as iron ore, mill scale, corroded scrap iron and limestone.

Various controls are used to produce the type of steel desired. These include temperature, rate of heating or cooling, time of treating, and materials added to the metal.

The finished molten steel is drawn from the furnace to ladles where it may receive any of numerous additives. These are materials that impart special characteristics to the finished steel.

From the ladles the molten steel is "teemed" or poured into forms in which it is allowed to cool and solidify. The large, solid steel blocks that result are called ingots.

26. Rolling

The remainder of the processing at the Ecorse plant is the rolling of the ingots to change them from blocks to the finished products such as sheets, strips, bars, rods and various structural forms. There are several auxiliary

processes, of which acid pickling is important in the production of waste.

Briefly, rolling is a process of passing the steel, usually hot to permit more rapid changes in shape, between pairs of cylindrical rolls revolving in opposite directions. Pressure exerted on the rolls compresses the steel, usually reducing its thickness and increasing its length and width.

Straight cylindrical rolls produce flat forms such as sheets and strips. Others than flat forms, such as bars, rods, I-beams and other structural forms, are produced by cylindrical rolls with variously shaped concentric grooves or "passes" in the surfaces of rolls.

It is not possible to reduce the large ingots to thin sheets or small bars in a single pair of rolls. The ingots pass through a great many rolls which successively reduce the cross sections of the forms to produce the desired finished shapes.

Two principal wastes are common to all the rolling processes. The surface of the hot steel oxidizes rapidly to form a coating of iron oxide, or mill scale. This must be removed to prevent impairment of the quality of the finished product. Several methods are used. Some of the sale flakes off in the rolling process. Some is knocked loose by high pressure water sprays. Some is removed by intense local heating of the surface with gas flames which cause differential expansion and cracking of the scale. This process is called scarfing. This mill scale that is flaked off as solid particles drops into channels recessed in the floor below the rolling mills. It is transported by water to scale pits, where some of it settles out and is recovered for reprocessing in the furnaces. Some finer particles pass through the scale pits and are carried to the sewers and thence to the river.

The other waste common to all the rolling mills is lubricating greases and

oil. The heavy, high speed machinery used requires large amounts of lubricants. The Ecorse plant uses averages of 3,870 pounds of grease and 1,421 gallons of oil daily for lubrication. Some of this inevitably escapes to the sewer.

a. Blooming and Slabbing Mills

The ingots are reduced in cross section in one slabbing and two blooming mills. Slabs, generally, are rectangular in cross section and may vary from 2 to 6 inches in thickness, and from 24 to 60 inches in width. Blooms, generally, are square or slightly oblong in cross section, and may vary from 6 by 6 inches to 10 by 12 inches.

b. Bar and Billet Mill

The blooms go to a bar and billet mill, where they are further reduced in cross section to billets, generally ranging from 2 by 2 inches to 5 by 5 inches.

c. Merchant Mills

Two merchant mills receive the billets and roll them into bars, rods and other structural forms. The forms are batch pickled in sulfuric acid, sorted, and shipped.

d. Hot Strip Mills

The slabs go to two hot strip mills. They are passed successively through roughing, broadside, and finishing rolls that reduce the thick slabs to thin "breakdowns." These breakdowns may be cut into sheets or coiled, as strips, for shipment.

e. Cold Strip Mill

The portion of the breakdowns that are not sold as strips are pro-

cessed further in a cold rolling mill. They first pass through a bath of sulfuric acid where they are pickled to dissolve mill scale. This process is discussed separately below. After rinsing and drying the strip passes through levelers and side strippers to the cold rolls. Here soluble oil is sprayed on the rolls and the strip to reduce the heat produced by physical deformation of the metal under high pressures. An average of 2,174 gallons of oil per day is used. The rolled strip is then heat treated, oiled and shipped.

27. Pickling

As noted above, both Merchant mill and cold rolled strip products are pickled in strong sulfuric acid to dissolve and remove mill scale. Merchant mill products are pickled by the batch method, while strips for cold rolling are pickled by the continuous method.

The strong acid reacts with the iron oxide (mill scale) to form ferrous sulfate. As the ferrous sulfate concentration builds up the rate of reaction of sulfuric acid with the iron oxide slows down and treatment efficiency drops. When the rate of reaction becomes too slow the acid-ferrous sulfate solution must be discarded and replaced by fresh sulfuric acid. At the Ecorse plant 150 tons of 60°Be' acid are used daily.

The waste acid-ferrous sulfate solution is the waste pickle liquor common to steel mills.

At the Ecorse plant all pickling operations are in a single area, served by the No.3 sewer. The waste pickle liquor discharges to two pump sumps, from which it periodically is pumped to an acid proof tank formerly used for acid neutralization by addition of lime. This tank has an outlet orifice that affords a certain amount of restriction in discharge from the tank to the

acid sewer. The acid sewer (No.3A) discharges to the No.3 sewer about six feet from its entrance to the river.

The pumping system was intended to equalize discharge of the waste pickle liquor to the river, but was not accomplishing its purpose during the waste survey. The manually operated pumps were operated only two to three times during each shift. The equalization tank emptied after the pumps stopped and several hours might elapse, between pumping periods, when no waste liquor was being discharged. While the pumps operated the depth of liquor in the tank increased until the pumps again stopped. When the pumps stopped the depth of liquor was at a maximum for that pumping cycle. The variable liquid level and corresponding variable head, caused variations in rate of waste discharge. At times the discharge exceeded the capacity of the 12 inch acid sewer and a portion of the waste pickle liquor overflowed directly to the No.3 sewer at a point near the equalization tank.

In addition, the results of sample analysis indicated the presence of large quantities of acid and ferrous sulfate in sewer No.3 when there was no discharge from the equalization tank, and in sewer No.4, which was said not to receive any acid waste. Subsequent investigation revealed that acid leaking from pickling equipment and accumulating below the pickling building was being pumped to sewer No.3 at a point near the pickling area. An interconnection between sewers Nos. 3 and 4 permitted this acid waste to flow through both sewers to the river.

28. Oil Recovery

Sewer No.4, serving the cold roll mill, carries the waste oil used for cooling the rolls and the strip and some lubricating grease and oil. A portion of the oil is recovered in an oil separator built into the bank of the

river at the mouth of the sewer. Separator capacity is 8,000,000 million gallons, which provides 26 hours detention at the average 7.3 million gallons per day flow of waste in the sewer.

Sheet iron pilings were driven into the river bottom to form three sides of the oil separator, with the river bank serving as the fourth side. The separator has a submerged port, 10 by 12 feet, at the downstream end through which the effluent discharges to the river. The top of the port is approximately one foot below minimum water level in the river. Normal river level fluctuation at this point is 6.5 feet. A neoprene curtain wall 8'-10" high, is installed around the inside of the sheet metal piling to prevent leakage of oil from the separator. This curtain wall extends about 8 inches below minimum river level.

The water level in the separator is influenced by the level in the river. Rapid fluctuations in level, such as those due to waves caused by wind and by passing boats, appeared to reduce the efficiency of the oil separator and permit the escape of quantities of oil. On at least two occasions, while the survey was in progress, a blanket of oil covering possibly 200 to 300 square feet of river surface was observed immediately below the downstream end of the separator.

Oil is removed from the surfaces of the separator by a floating skimmer, and is pumped to an overhead tank. The pumps are operated two days weekly, usually on Tuesdays and Thursdays.

The recovered oil is hauled by tank truck to a storage tank where it is further dewatered.

SURVEY PROCEDURES

29. Sample Collection and Preservation

a. Blast Furnace Division

Samples of the plant water supply were collected from a cooling water line in the sludge vacuum filter building of the blast furnace dust recovery plant.

The blast furnace gas wash water waste was sampled in the influent distributor box at the Dorr Thickeners. At the start this was thought to include all wash waste water from all blast furnaces. During the survey it was discovered that a portion of the wash wastes from the B and C furnaces was bypassing the pumping station which lifts the wastes to the Thickeners and was flowing directly to the river through a cross-over into sewer No.2. Efforts to stop the leak causing this were unsuccessful, and a portion of the waste continued to by-pass the pumping station through the first week of sampling. Subsequently the leak was stopped completely and additional samples were collected.

The effluent from the Dorr Thickeners was collected from the first manhole on sewer No.4 below the manhole in which the effluent from the two Thickeners joined. This did not include the waste water from the vacuum filters, which was quite clear and was estimated to be less than one-half of one per cent of the flow from the Thickeners.

Samples were collected by plant operating personnel at hourly intervals. Equal hourly portions were composited for each 24 hour period, starting at 8:00 AM on May 1 and ending at 7:00 AM on May 6, 1955. Additional composite samples were collected for 24 hours each during May 22-23, and 24-25.

Sodium hydroxide was used to stabilize samples for phenol, cyanide and thiocyanate determinations. Acid was used to preserve samples for determination of ammonia. Unpreserved samples were collected for other analyses.

Samples were divided and portions were furnished to the Blast Furnace Division laboratory.

b. Ecorse Plant

Samples of the plant water supply were collected from a line discharging near the equalization tank of the waste pickle liquor pumping system.

Sewer No. 1 was sampled at its mouth by dipping from a platform installed just above river water level. This sewer carried oily lubricating wastes and mill scale from the No. 3 slabbing mill and motor room. Before the waste reached the sampling point it passed through a scale pit which was equipped for oil removal. It was not feasible to measure the flow to the scale pit, and no attempt was made to sample it to determine efficiency of the pit. Recirculation of a portion of the effluent back to the pit, by the pumps discharging the waste to the sewer, caused the rates of influent and effluent flow to differ. Flow measurements at the mouth of the sewer were not applicable to instantaneous influent flow.

Sewer No. 3 was sampled near its mouth by dipping at a point just above the entrance of the waste pickle liquor sewer discharge. A platform was provided here also. Samples were omitted when discharge of the waste pickle liquor was at a maximum, to avoid inclusion in the composite of pickle liquor that overflowed into sewer No.3 at the equalization tank. This sewer carried oily lubricating waste and mill scale from a hot strip mill and a blooming mill, and waste water from the pickling building. The sewer was not thought to carry waste pickle liquor at this sampling point but, as previously dis-

cussed, pickling equipment leaks in the pickling area contributed large amounts of acid and ferrous sulfate to the sewer above this point.

The waste pickle liquor was sampled by dipping in one of the two pump sumps which were reported to receive all pickle liquor. Both sumps were served by a single waste line which split just before it reached the sumps.

Sewer No. 4 was sampled from a small pump temporarily installed at the effluent end of the oil separator near the middle of the effluent port. This sewer carried large quantities of soluble cooling oil as well as oily lubricating wastes and mill scale from the cold rolling mill. The influent velocity to the oil separator was too low to keep the oil uniformly mixed and representative sampling of the influent waste was not possible. This sewer was not thought to carry acid wastes, but a portion of the leaks from the pickling equipment flowed into it and contributed large amounts of acid and ferrous sulfate.

Two special oil samples were collected from the overhead oil tank at the oil separator.

Samples were collected by plant operating personnel at hourly intervals. Equal hourly portions were composited for each 24 hour period, starting at 8:00 AM on May 8 and ending at 7:00 AM on May 13, 1955. No preservation was necessary for any of the constituents involved. Special test tube samplers were used for oil samples at sewers Nos. 1 and 4. The samplers had glass tubes for sample inlet and air outlet adjusted to stop sample inflow when about 30 ml had been collected. The entire 30 ml portions were transferred to glass stoppered liter bottles. The test tubes and sample bottles used for each oil sample composite were washed with solvent and added to the sample during the procedure for oil determination.

30. Flow Measurements

a. Blast Furnace Division

Flow to and from the Dorr Thickeners were assumed to be the same. No allowance was made for the small volume of sludge withdrawn from the bottoms of the Thickeners.

Data on flow were obtained from recording charts on the blast furnace gas wash water supplied to the washers serving furnaces B, C and D. In addition, spot manometer readings on flow to all electrostatic precipitators for the three furnaces were made at irregular intervals. These were read with sufficient frequency to make certain that the flow was reasonably uniform. The manometers were read routinely by plant personnel, and flows were adjusted manually as necessary. No method of measuring the relatively small flows to the septum valves, ahead of the precipitators, was readily available. These were omitted from the total flow values.

This method of obtaining flow data was based on the assumption that all water used for gas cleaning was going to the Thickeners. As previously noted, a significant portion of the water used at furnaces B and C was found to be by-passing the pumps directly to the river during the first week of sampling. For this reason the flow values were higher, by indeterminate quantities, than the actual flows going to the Thickeners. This error was not so serious as it might appear at first. The concentrations of soluble constituents were not affected significantly by passage of the waste through the Thickeners. The concentrations of soluble materials in the waste by-passing the Thickeners should have been essentially the same as those in the waste going through the Thickeners. The daily weights of soluble materials were calculated on the basis of concentrations of constituents in the Thickener effluent and the

total gas wash water waste flow. This should represent reliable values for the soluble materials discharged to the river regardless of the fact that a portion of the waste by-passed the Thickeners.

This hypothesis does not apply to values for insoluble materials. These include total and unsettleable suspended solids, and that portion of the alkalinity which was due to suspended calcium carbonate. The concentrations of suspended materials in the Thickener effluent were much lower than those in the waste by-passing directly to the river. Therefore, the total daily weights of suspended materials actually going to the river before the leak was stopped were much higher than amounts calculated from total waste flow and Thickener effluent concentrations. On the other hand, the calculated daily weights should be reasonably representative of the amounts of those materials that would have gone to the river if all wastes had been passing through the Thickeners. The amounts probably are somewhat low since the reduced flow to the Thickeners permitted longer detention and probably resulted in greater settling efficiency in the Thickeners.

b. Ecorse Plant

Flow measurements were made by current meter at the mouths of sewers Nos. 1 and 3. Measurements were made once or twice daily during the survey. It was not feasible to measure the flow through the effluent port or at the influent end of the oil separator on sewer No. 4. Two current meter measurements were made on separate days in a manhole on sewer No. 4 south of the middle of skull cracker building No. 1.

Flow of waste pickle liquor was calculated from records kept by operators at the pump building. They recorded the rises in waste levels in the two pump sumps during periods when the pumps were not operating, and the times that the

pumps were started and stopped. Average rates of inflow for the daily periods when the pumps were not operating were calculated from total non-pumping time, total waste level rise, and sump cross sectional areas. These average rates were used to compute total flows for the full 24 hour periods. Since the pump operation averaged only 2.5 hours per day during the waste survey it is felt that this method yielded acceptable values.

31. Laboratory Procedures

a. Blast Furnace Division

The following determinations were made on the daily composites collected during the first week:

Phenols
Ammonia
Cyanides
Thiocyanates
pH
Alkalinity
Iron
  Total
  Ferrous
Suspended Solids
  Total
  Unsettleable

In addition fluorides were determined on the Thickener effluent composites.

On the special samples collected during May 22-23 and 24-25 the chief interest was in suspended solids when all gas wash water was passing through the Thickeners. In addition, phenols were determined on the plant water supply and the Thickener effluent on the May 22-23 composite.

Laboratory methods used and the pollutional significance of the constituents determined are described in the Appendix.

b. Ecorse Plant

The following deteminations were made on the daily composites:

	Plant Water Supply	Sewer No. 1	Sewer No. 3	Sewer No.3A	Sewer No. 4
Oils	X	X			X
Suspended Solids					
Total	X	X	X	X	X
Unsettleable	X	X	X	X	X
Iron					
Total	X	X	X	X	X
Soluble	X	X	X	X	X
Acidity					
Total			X	X	X
Mineral			X	X	X
Alkalinity	X	X			
pH	X	X	X	X	X

QUANTITY AND CHARACTER OF WASTES

32. Presentation of Data

The daily and average results of laboratory analyses and of flow measurements are presented in Tables 1 and 2 of the Appendix. The pounds per day of materials carried in the water supply, and the pounds per day added by the processes are given in Tables 3 and 4. Amounts added by the process were computed by subtracting amounts in the water supply from those found in the sewers.

33. Discussion of Data

a. Blast Furnace Division

Results in Table 3 show that the wastes from the gas washing operations were contributing an average of 54 pounds of phenols per day to the river. The phenol found in the Thickener effluent was believed to be absorbed by the coke from the contaminated quench water and liberated from the coke into the blast furnace gas. The gas furnace gas wash water then absorbed the phenol from the gas and carried it to the river. During the period when the plant gas wash water effluent was sampled all ammonia still wastes and other contaminated wastes from plant No. 2, and the ammonia concentrator and light oil recovery wastes from Plant No. 1 were entering the quench water system. However, not all of the waste was evaporated by coke quenching. A considerable overflow from the east quench station was carried to the Detroit River through outlet No. 3 of the Zug Island Plant. About 120 gallons per minute or 25 per cent of the quench water system supply was estimated to have overflowed during the survey. Occurrence of the overflow was not discovered until near the end of the survey, and characteristics of the overflow were not determined. The rate of overflow was measured after completion of the survey.

Several factors were thought to cause this failure of the system to consume the wastes. The relatively clean condenser water from the ammonia concentrator at the No. 1 coke plant contributed an appreciable volume of uncontaminated water to the system which made it more difficult to distribute to the quench stations, and to keep the system in balance so no overflow occurred. Also it appears necessary to provide some equalizing tank capacity for the wastes and return quench water and to maintain closer control of addition of uncontaminated makeup water to the system.

The company intends to provide the necessary piping changes equalizing tank capacity and other equipment necessary to close the quench water system and assure consumption of all contaminated coke plant wastes.

The closure of the quench water system probably will increase slightly the quantity of phenols in the blast furnace gas wash water. More phenols will be applied to the coke in quenching and the carryover should be greater. This increase can be minimized by improved operation of the dephenolization unit. Plant records indicate that the unit's phenol recovery efficiency averaged only 88.2 per cent during the period that the Thickener effluent was sampled. During the special study of coke plant waste disposal and phenol carryover the dephenolization plant averaged nearly 96 per cent recovery.

There is a difference between the quantity of phenols found in the blast furnace gas wash water in the total effluent study (54 pounds per day), and the quantity predicted to be present in the total gas wash water wastes from the special phenol carryover study at Blast Furnace D (48 pounds per day). The predicted value was partly based on an estimate of the quantity of phenols contributed by the ammonia liquor concentrator wastes from plant No.1. This estimate may be in error. In addition, the computations by which the predicted value was obtained assumed 95.5 per cent phenol recovery by dephenolization.

The special study of carryover of contaminants to the blast furnace gas wash water indicated that there was no correlation between ammonia and cyanides in the quench water supply and in the gas wash water waste. The results reported for the blast furnace gas wash water effluent probably will be little affected by the proposed changes in the quenching system. These show a discharge to the river of 671 pounds of ammonia, 136 pounds of thiocyanates, and 74 pounds of cyanides per day.

The ammonia stills were being operated experimentally in an attempt to achieve the most effective method of ammonia recovery. Recoveries were erratic during this period. Improvement in ammonia recovery probably will be reflected in reduced ammonia in the gas wash water waste.

The efficiency of suspended solids removal by sedimentation of blast furnace gas wash water wastes varied widely during the survey. Average net reductions of total suspended solids was 84.5 per cent during the first five days of the study and of settleable solids 85.1 per cent. The following tabulation gives the daily net reductions:

	Suspended Solids Removal-Per Cent	
Date	Total Suspended Solids	Settleable Solids
5/1/55	97.2	97.3
5/2/55	96.1	96.6
5/3/55	81.8	82.4
5/4/55	68.5	69.2
5/5/55	79.1	79.8

The efficiencies for May 1 and 2 were similar to those previously found by the plant laboratory. Following the finding that a portion of the gas wash water waste was by-passing the Thickeners, partial stoppage of the leak was accomplished on May 3. Total suspended solids removal efficiency then dropped off to about 80 per cent, with a low of 68.5 per cent on one day. Unsettleable suspended solids removal was even more erratic, with an increase indicated on one day.

When appraised of these findings company personnel investigated the settling units and concluded that two factors probably accounted for their poor performance. Several of the risers were partially clogged in both Thickeners, causing excessive overflow at high velocities through the unclogged risers.

This resulted in poor distribution of flow through the Thickeners, with lowered settling efficiencies.

In addition it was found that at times there was direct passage of a portion of the influent flow over the low peripheral wall (freeboard) of the settling units into the amular effluent collecting channel. This occurred especially during periods of high wind.

The clogged risers were cleaned. The residual overflow of gas washer water waste that had been by-passing the pumps to the Thickeners was stopped. On May 22 and 24 additional checks on efficiency of solids removal were made. The efficiency of solids removal on these two dates is shown in the following tabulation:

	Suspended Solids Removal-Per Cent	
Date	Total	Settleable
5/22/55	85.2	85.6
5/24/55	92.4	93.5
Avg.	88.8	89.6

This represented some improvement over the results for the period May 3-5, but did not equal the efficiency formerly found by the plant laboratory.

Total iron removal in the Thickeners closely paralleled that for total suspended solids, generally being a few per cent lower. During the last three days the average daily loss of total iron (as Fe) to the river through the thickeners was 45,000 pounds per day. This was the equivalent of 32 tons per day of hematite ore (Fe_2O_3).

The ferrous iron in the waste was unimportant.

Fluorides were of little significance, averaging only 1.37 ppm in the waste.

b. Ecorse Plant

Oils were determined in the water supply and in two sewers. A total of 8,400 pounds per day was discharged to the river from plant processes at the No. 3 blooming mill and the cold rolling mill. Of this, 8,310 pounds per day was from the oil separator on the cold mill sewer (No. 4). Special samples of the oil pumped from the separator were collected on two days. These contained 2.10 and 4.26 pounds of oil per gallon of sample, or an average of 3.18 pounds per gallon. Company personnel stated that oil pumpage from the separator averaged 32,000 gallons per week. On this basis oil recovery averaged about 101,800 pounds per week or 14,540 pounds per day. The estimated oil recovered plus the oil carried in the separator effluent totaled 22,850 pounds per day. This indicates an oil recovery efficiency of 63.6 per cent. These values are approximations only, due to the highly erratic composition of the oil pumped from the separator, and the difficulty of obtaining representative samples.

The separator accomplished better oil recovery than had been anticipated, since most of the oil involved was soluble. Two factors probably contributed to this. Some soluble oil emulsions break when diluted sufficiently with water. The flow in sewer No. 4 diluted the oil by a factor of several thousand. In addition, pickle liquor that had leaked into this sewer reduced the pH to an average of 2.34, which probably played an important part in breaking the emulsion.

The waste in three of the four sewers was acid, with only the No. 3 blooming mill waste (sewer No. 1) exhibiting alkalinity normal to the plant water supply.

All of the sulfuric acid used in the pickling process should be reflected in the waste data as free mineral acid, as iron from the reaction between the acid and mill scale, and as reduction in natural alkalinity of the water supply. The values for acidity added by the process in Table 4 are the sums of pounds per day of mineral acidity determined by analysis of the wastes and of natural alkalinity of the water supply. The total of 208,900 pounds per day, in sewers Nos. 3, 3A and 4, is reported as equivalent calcium carbonate. This is equivalent to 204,700 pounds per day of sulfuric acid. In addition the three wastes contained a total of 40,500 pounds per day of soluble iron, which is assumed to be ferrous iron. It would have required 71,100 pounds of sulfuric acid per day to react with this amount of iron. These data account for a total of 275,800 pounds, or 137.9 tons, of 100 per cent sulfuric acid per day. The plant uses an average of 150 tons of 66°Be' commercial acid per day, which is equivalent to 139.8 tons of 100 per cent sulfuric acid. The agreement between the two figures, with a difference of only 1.36 per cent, is remarkably good.

The difference between total (43,700 pounds per day) and soluble (40,500 pounds per day) iron in all sewers was suspended iron, which probably was mill scale. This 3,200 pounds per day in the total 68.3 million gallons per day flow from all sewers is equivalent to 5.6 ppm of iron. This indicates good efficiency in recovery of mill scale.

Total suspended solids of 19,800 pounds per day included the above mill scale which, calculated as FeO, was 4,130 pounds per day. Some oil probably was included in the remaining 15,670 pounds per day. Of this, 12,500 pounds per day, or 80 per cent, was in the hot strip mill sewer (sewer No. 3).

The pH values (Table 2) in general confirmed the results of acidity and

alkalinity determinations. The sewers carrying the pickle liquor wastes yielded pH values below 4.5, which is evidence of mineral acidity. Damage to sewers has been found in lines carrying wastes with pH less than 5.0.

CONTEMPLATED CHANGES IN PRODUCTION AND CONTROL OF WASTES

34. Increased Production

A new furnace was being installed during the survey to replace the old A furnace. When placed in operation it should increase pig iron production by at least 35 per cent.

This should result in a corresponding increase in blast furnace gas wash water waste. The erratic performance of the settling units, and the low efficiencies found at times during the survey, makes it questionable whether the existing units have adequate capacity to accept the added volume of wash water waste. Consideration was being given to raising the free board of the Thickeners to prevent short circuiting of the wash water across the surfaces of the Thickeners directly into the effluent troughs. This improvement should help to accommodate the increased flow from the new blast furnace.

Coke production during the survey was well in excess of the blast furnace requirements at that time. No increase in coking, with resulting wastes from this source, is anticipated because of the increase in pig iron production.

The increased pig iron produced is expected to be reflected in increased production at the Ecorse plant, with attendant increases in wastes discharged to the river there. Insufficient data on present and anticipated production at Ecorse are available to permit quantitative evaluations of the probable increases.

35. Oil Recovery

It was planned to reduce the size of the outlet port of the oil separator on No. 4 sewer at the Ecorse plant from 10 by 12 feet to about 3 by 4 feet. Plant engineers believe that this would increase efficiency of oil recovery by reducing disturbances caused by wave action on the river.

Consideration was being given to a change from soluble to insoluble oil for cooling in the cold rolling mill. If adopted, this change should increase the efficiency of the oil separator.

Company personnel said waste pickle liquor would be eliminated from No. 4 sewer. If use of soluble oil for cooling is continued elimination of the acid probably would reduce the efficiency of the oil separator.

Plans were under way to install oil separators on sewers No. 2 and 3 at the Ecorse plant. This would reduce the total oil discharged to the river.

36. Waste Pickle Liquor Disposal

Company officials said that the pump operators would be instructed to increase the frequency of pumping the waste pickle liquor from the acid pump sumps to the equalization tank. This should assure a lower and more nearly uniform rate of flow of waste acid to the river and increase the effectiveness of neutralization by the natural alkalinity of the river water.

Plans were under way to install new pickling equipment. This should eliminate the leaks that caused waste pickle liquor to enter sewers Nos. 3 and 4.

37. Improved Operation of Ammonia Stills

Improved efficiency of ammonia recovery was the objective of the experimental operation of the ammonia stills at coke plant No. 2 during the survey.

If this objective were achieved it would reduce the ammonia loss to the river in any coke plant wastes that might not be consumed in quenching. It should be reflected in lower loss of ammonia in blast furnace gas wash water waste.

38. Improvement in Carbolate Quality

During the period covered by the survey, it was necessary to shut down the weak ammonia liquor dephenolization equipment at the Blast Furnace Division at times. This resulted in an increase in phenols in the plant wastes. The carbolate being produced at that time contained impurities that limited its market in competition with higher quality synthetic phenol. When carbolate production exceeded sales and storage facilities were full it was necessary to close down the dephenolization plant.

Efforts were being made to improve carbolate quality and increase its potential market to permit full time operation of the dephenolization plant.

39. Contaminated Water System Changes

Consideration was being given to elimination from the contaminated water system of cooling water used in the ammonia condenser at the No. 1 by-products plant of the Blast Furnace Division. If done, this should permit operation of the contaminated system on a completely closed basis, and avoid overflow of excess waste water to the river at the No. 1 coke plant. It should reduce the phenols, ammonia, cyanides, and thiocyanates discharged to the river.

40. Waste Sampling Program

Thought was being given to initiating a routine waste sampling program at both Great Lakes Steel Corporation plants. Such a program would permit early detection of certain irregularities in plant operations and waste disposal and thus make the waste control program more effective.

APPENDIX A

TABULATION OF DATA

TABLE 1

ANALYTICAL DATA ON WASTES AND WATER SUPPLY
BLAST FURNACE GAS WASH WATER
ZUG ISLAND PLANT
GREAT LAKES STEEL CORPORATION

Source of Sample	Date of Sample	Phenols ppm	Ammonia (as N) ppm	Thiocyanates (as CN) ppm	Cyanides (as CN) ppm	pH	Alkalinity (as $CaCO_3$) ppm	Iron (as Fe) ppm		Suspended Solids, ppm		Fluorides ppm	Flow M.G.D.
								Total	Ferrous	Total	Unsettleable		
Plant Water Supply	5/1/55	0.022	0.52	0.02	0.027	7.9	85	0.26	0.09	18.0	9.8	-	-
	5/2/55	0.450	0.43	0.02	0.017	7.7	84	0.68	0.07	9.6	5.0	-	-
	5/3/55	0.009	0.79	0.0	0.039	8.1	85	2.48	0.07	19.8	17.2	-	-
	5/4/55	0.026	0.78	0.05	0.031	8.1	84	2.76	0.01	16.2	6.2	-	-
	5/5/55	0.012	1.00	0.009	0.053	7.1*	67*	1.86	0.03	13.0	11.0	-	-
Average		0.104	0.70	0.02	0.033	7.8	81	1.61	0.05	15.3	9.8	-	-
Thickener Influent	5/1/55	0.88	4.56	1.3	0.736	8.3	988	1,350	0.44	4,726	60.8	-	14.77
	5/2/55	0.58	6.20	1.4	0.602	8.1	790	1,020	0.11	4,799	48.8	-	14.80
	5/3/55	0.36	4.90	1.1	0.608	8.1	1,270	1,460	0.11	5,852	58.0	-	14.72
	5/4/55	0.42	7.20	1.1	0.552	7.9	1,040	1,400	0.07	5,510	59.2	-	14.73
	5/5/55	0.58	3.30	1.3	0.720	8.1	1,010	1,330	0.05	5,294	126	-	14.80
Average		0.56	5.23	1.24	0.644	8.1	1,020	1,312	0.16	5,236	70.6	-	14.76
Thickener Effluent	5/1/55	0.88	5.76	1.2	0.648	7.8	220	46	0.39	142	22.4	0.84	14.77
	5/2/55	0.58	5.80	1.2	0.586	8.1	220	40	0.23	191	28.8	0.96	14.80
	5/3/55	0.35	6.40	1.0	0.652	7.8	430	300	0.28	1,078	54.4	1.54	14.72
	5/4/55	0.49	7.60	1.0	0.584	7.9	520	460	0.20	1,738	61.2	1.88	14.73
	5/5/55	0.38	5.20	1.2	0.720	7.9	400	338	0.11	1,117	73.6	1.64	14.80
Average		0.54	6.15	1.12	0.638	7.9	358	237	0.24	853	48.1	1.37	14.76
SPECIAL SAMPLES													
Plant Water Supply	5/22/55	0.10	0.27	-	-	-	-	-	-	18.4	6.8	-	-
	5/24/55	-	-	-	-	-	-	-	-	35.4	8.4	-	-
Thickener Influent	5/22/55	-	-	-	-	-	-	-	-	5,934	72.0	-	14.86
	5/24/55	-	-	-	-	-	-	-	-	4,704	80.0	-	14.80
Thickener Effluent	5/22/55	0.91	-	-	-	-	-	-	-	886	48.0	-	14.86
	5/24/55	-	-	-	-	-	-	-	-	363	36.0	-	14.80

* Sample apparently contaminated with acid in collection.

TABLE 2

ANALYTICAL DATA ON WASTES AND WATER SUPPLY
ROLLING MILL WASTES AND PICKLE LIQUOR
ECORSE PLANT
GREAT LAKES STEEL CORPORATION

Source of Sample	Date of Sample	Oils ppm	Suspended Solids - ppm		Iron - ppm		Acidity (as $CaCO_3$) - ppm		Alkalinity (as $CaCO_3$) ppm	pH	Flow M.G.D.
			Total	Unsettleable	Total	Soluble	Mineral	Total			
Plant Water Supply	5/8/55	18.2	19.6	18.0	1.56	0.48	-	-	88	7.7	
	5/9/55	7.3	23.2	14.0	1.74	0.39	-	-	89	7.7	
	5/10/55	4.3	22.0	14.8	1.78	0.32	-	-	91	7.7	
	5/11/55	3.3	16.8	16.0	1.86	0.47	-	-	89	7.8	
	5/12/55	4.3	15.6	13.2	1.94	0.30	-	-	88	7.6	
Average		7.5	19.4	15.2	1.78	0.39	-	-	89	7.7	-
Sewer No.1 (Scale and Oil Separator Effluent)	5/8/55	10.4	39.5	15.2	3.74	0.46	-	-	88	7.8	
	5/9/55	10.5	45.5	16.4	3.84	0.39	-	-	89	7.7	
	5/10/55	10.2	63.2	10.8	4.52	0.29	-	-	90	7.7	
	5/11/55	5.6	12.0	11.0	1.78	0.29	-	-	89	7.9	
	5/12/55	8.8	23.0	8.0	2.26	0.31	-	-	88	7.6	
Average		9.1	36.6	12.3	3.23	0.35	-	-	89	7.74	6.73
Sewer No.3 (Above Point of Pickle Liquor Discharge)	5/8/55	-	67.0	24.0	17.6	4.70	-	-	32	6.4	
	5/9/55	-	46.8	23.2	28.6	23.0	36	100	-	3.4	
	5/10/55	-	50.4	29.2	19.4	17.1	21	74	-	3.5	
	5/11/55	-	51.0	29.5	17.8	17.7	17	75	-	3.6	
	5/12/55	-	43.6	27.6	44.4	36.1	145	250	-	2.7	
Average		-	51.8	26.7	25.6	19.7	54.8	125	-	3.92	54.0
Sewer No.3A (Waste Acid Pickle Liquor Pit)	5/8/55	-	42.0	38.0	8,650	8,600	49,200	60,000	-	0.6	
	5/9/55	-	73.0	45.6	13,600	13,250	57,100	72,300	-	0.5	
	5/10/55	-	93.2	60.8	14,800	14,600	60,800	81,600	-	0.4	
	5/11/55	-	80.0	72.4	12,200	11,900	50,800	67,300	-	0.55	
	5/12/55	-	74.0	50.5	16,800	16,350	57,500	81,100	-	0.5	
Average		-	72.4	53.5	13,210	12,940	55,080	72,460	-	0.51	0.249
Sewer No.4 (Oil Separator Effluent)	5/8/55	57.3	94.8	59.2	64.0	60.8	314	394	-	2.4	
	5/9/55	174	112	76.8	110	94.5	492	616	-	2.2	
	5/10/55	155	74.0	66.8	120	108	504	664	-	2.3	
	5/11/55	179	99.0	58.0	77.0	63.5	260	351	-	2.5	
	5/12/55	154	52.0	47.0	83.0	77.5	396	520	-	2.3	
Average		144	86.4	61.6	90.8	80.9	393	509	-	2.34	7.30

TABLE 3

QUANTITY OF POLLUTIONAL CONSTITUENTS
BLAST FURNACE GAS WASH WATER
ZUG ISLAND PLANT
GREAT LAKES STEEL CORPORATION

Source of Sample	Date of Samples	Phenols #/Day	Ammonia (as N) #/Day	Oils #/Day	Thiocyanates (as CN) #/Day	Cyanides (As CN) #/Day	Alkalinity (as $CaCO_3$) #/Day	Suspended Solids #/Day		Iron (as Fe) #/Day		Fluorides #/Day	Flow M.G.D.
								Total	Unsettleable	Total	Ferrous		
Plant Water Supply	5/1-5/55	12.8	86.2	-	2.5	4.06	9,970	18,800	1,210	198	6.2	-	14.76
Thickener Influent	5/1-5/55												14.76
Total in Sewer		68.9	644	-	153	79.3	125,600	645,000	8,690	161,500	19.7	-	
Added by Process		56.1	558	-	150	75.2	115,600	626,000	7,480	161,300	13.5	-	
Thickener Effluent	5/1-5/55												14.76
Total in Sewer		66.5	757	-	138	78.5	44,100	105,000	5,920	29,500	29.5	.69	
Added by Process		53.7	671	-	136	74.4	34,100	86,200	4,710	29,300	23.3		

TABLE 4
QUANTITY OF POLLUTIONAL CONSTITUENTS
ROLLING MILL WASTES AND PICKLE LIQUOR
ECORSE PLANT
GREAT LAKES STEEL CORPORATION

Source of Sample	Dates of Samples	Oils #/Day	Alkalinity (As $CaCO_3$) #/Day	Acidity (As $CaCO_3$)-#/Day		Suspended Solids #/Day		Iron (as Fe) #/Day		Flow MGD
				Mineral	Total	Total	Unsettleable	Total	Ferrous	
Plant Water Supply	5/8-12/55									
Sewer Involved:										
No.1		421	4,990	-	-	1,090	853	100	21.9	6.73
No.3		-	-	-40,100*	-40,100*	8,740	6,850	802	176	54.0
No.3A		-	-	-185*	-185*	40	32	4	0.8	0.249
No.4		457	-	-5420*	-5,420*	1,180	926	108	23.8	7.30
Totals		878	4,990	-45,700*	-45,700*	11,050	8,660	1,014	222	68.3
Sewer No.1										
Total in Sewer		511	4,990	-	-	2,050	690	181	19.6	6.73
Added by Process		90	0	-	-	960	-163	81	2.3	
Sewer No.3										
Total in Sewer		-	-	24,700	56,300	23,300	12,000	11,500	8,870	54.0
Added by Process		-	-	64,800	96,400	14,600	5,150	10,700	8,690	
Sewer No.3A										
Total in Sewer		-	-	114,600	150,700	151	111	27,500	26,900	0.249
Added by Process		-	-	114,800	150,900	111	79	27,500	26,900	
Sewer No.4										
Total in Sewer		8,770	-	23,900	31,000	5,260	3,750	5,530	4,930	7.30
Added by Process		8,310	-	29,300	36,400	4,080	2,820	5,420	4,910	
Total Sewers 1,3,3A,& 4										
Total in Sewers		9,280	4,990	163,200	238,000	30,800	16,600	44,700	40,700	68.3
Added by Process		8,400	-	208,900	283,700	19,800	8,050	43,700	40,500	

*Negative acidity is equivalent weight of natural alkalinity of plant water supply neutralized by waste acid.

APPENDIX B

ANALYSES PERFORMED, SIGNIFICANCE, AND METHOD

The characteristics for which the samples were analyzed are listed and discussed in paragraphs following:

a. Phenols

For analytical purposes the term "Phenol" is used in a collective sense and includes those hydroxy derivatives of benzene which can be determined under specified conditions by the 4-aminoantipyrine method. The percentage composition of the various phenol-like compounds present in a given sample was not determined and any colors produced by the reaction of phenol-like compounds, as well as phenols, is reported as phenols. The colors produced by other phenol-like compounds are less intense than those from like concentrations of phenol, therefore the values expressed are the minimum concentration of phenol-like compounds present in the sample.

Phenols may cause tastes and odors in water supplies. Concentrations of as low as 0.002 to 0.005 ppm phenols may produce medicinal tastes and odors in the presence of chlorine in water. A concentration of 0.1 ppm of phenol alone will impart the characteristic taste and odor of phenol to water. Phenolic compounds are toxic to aquatic life, with lethal limits being dependent on such factors as concentration, time of exposure, and the chemical and physical characteristics of the water. The minimum concentration of phenol reported as being toxic to fish is 0.4 ppm. Fish exposed to phenolic compounds in water will acquire the tastes and odors of these compounds.

The colorimetric 4-aminoantipyrine method was used for the analysis as described in the reference below. Interferring substances were considered to be removed sufficiently by distillation from an acid solution. In many cases the concentration of phenols was read on the first distillate. In other cases, particularly for the lower concentrations, the distillate was extracted with chloroform and phenols read in the chloroform. A photometer was used for the readings.

Reference: M. B. Ettinger, C. C. Ruchhoft, and R. J. Lishka, Anal. Chem., 23, 1783 (1951).

b. Cyanide

The presence of cyanide in water has a significant effect upon biological activity; the toxicity limits are affected by water quality, temperature, type and size of organism, and cyanide compound present. Cyanides may exist in water as simple salts, double salts or complex forms. The simple salts of sodium, potassium or ammonia are quite soluble and very toxic. The double salts or complex forms show varying degrees of reactivity. Tests have shown that cyanide compounds have been toxic to fish in concentrations as low as 0.05 ppm as CN. Micro-organisms responsible for self-purification have been shown to be inhibited by a CN^- as low as 0.3 ppm.

The pyridine-pyrazolone colorimetric method was employed for concentrations below 1 ppm and the silver nitrate titration using rhodamine indicator

for higher concentrations.

Reference: Ludzack, R. J., Moore, W. A., and Ruchhoft, C. C., Anal. Chem., 26, 1784 (1954).

c. Thiocyanates

Thiocyanates have been reported as being relatively nontoxic to aquatic life. There has been speculation that the thiocyanates could be reduced to cyanides in the stream under certain conditions.

Thiocyanate was determined by the colorimetric procedure using benzidine pyridine color development and extraction as outlined by Nusbaum and Skupeko. This method measures both CN^- and CNS^-. The cyanide concentration measured by distillation and a separate test as outlined in the preceding paragraphs was subtracted to obtain the thiocyanate. Other interference was generally negligible because of the dilution and color extraction.

Reference: Nusbaum, I., and Skupeko, P., "Determination of Cyanides in Sewage and Polluted Water," Sewage and Industrial Wastes, 23, 875 (1951).

d. Ammonia

The toxicity of ammonium compounds is markedly influenced by the ammonia content existing as undissociated ammonium hydroxide, which is affected by the pH of the solution. At higher pHs ammonia may be toxic in concentrations of the order of 2 ppm. A synergistic toxic action of ammonia and cyanide in mixture has been demonstrated. In the treatment of water supplies ammonia combines with the chlorine added for disinfection, forming chloramines. Chloramines are not as effective as chlorine for sterilization, and larger doses are necessary. In water plants using breakpoint chlorination or chlorine dioxide treatment the ammonia present is oxidized by the disinfectant. Ammonia increases the quantity of disinfectants necessary.

The method of analysis used determines the ammonia present in the form of dissolved gas, ammonium hydroxide, and ammonium salts, such as ammonium chlorides, sulfates, or carbonates. It does not include albuminoid ammonia or organic ammonia compounds such as urea.

Reference: Standard Methods for the Examination of Water and Sewage, Tenth Edition, American Public Health Association.

e. pH

The symbol pH denotes the negative logarithm (to the base 10) of the hydrogen ion concentration of a solution, this symbol being a universal one in chemistry. The pH indicates the relative acidity or alkalinity of a water or waste, being lower with higher degrees of acidity.

Water with pH in either the upper or lower extremes may be toxic to aquatic life and may be corrosive or more expensive to treat for industrial or domestic uses. The International Joint Commission Objectives in regard to pH are that the water in the streams and lakes following initial dilution should not be less than 6.7 nore more than 8.5.

Reference: Standard Methods for the Examination of Water and Sewage, Tenth Edition. American Public Health Association.

f. Oils

This determination is a measure of materials extractable with a mixture of chloroform and carbon tetrachloride. In the wastes from the Ecorse plant the extractable materials would be expected to consist almost entirely of oils used in the process. In the analytical procedure the chloroform and carbon tetrachloride extract is evaporated under controlled temperature conditions and the residue weighed. During the evaporation of the chloroform and carbon tetrachloride in the analytical tests any highly volatile oil which may be extracted is also evaporated. The nature of the oil normally used in rolling mills is such that no highly volatile oils would be expected in the wastes.

Oil is a serious deterrent to subsequent domestic or industrial use of the receiving water, and may necessitate special treatment for its removal. Waters used for domestic water supplies may be objectionable because of tastes and odors caused by oil. Oil may cause difficulties at water purification plants by coating filters and other equipment. Oil may appear as free oil, soluble oil, emulsified oil, or as a coating on suspended matter. Floating oil, even in small amounts, is easily detected because of the iridescent sheen it causes on the water surface. As little as 25 gallons of oil per square mile may be visible under most favorable light conditions. Such floating oil is aesthetically offensive and may render the water useless for bathing and recreational uses. Oil coatings on water front structures, piers, piling, and ships hulls are objectionable and may constitute a fire hazard. Oil coatings on beach sands will destroy their recreational value. Wildfowl may be disabled if their feathers become saturated by contact with floating oil and will subsequently die from hunger, exposure, or drowning. Oil coatings on water surfaces reduce reaeration of waters unsaturated with oxygen. The oil may coat suspended matter which subsequently blankets the stream with an oily sludge.

Reference: Determination of Oil Content of Waste Waters, modified Sun Oil Company method.

g. Suspended Solids and Unsettleable Suspended Solids

Suspended solids are materials in suspension or floating on the surface of the wastes which are removed by the filtration process employed in the test.

The size and density of some suspended matter is such that it would readily settle out under suitable conditions of quiescence. Other material may be so fine that it would remain in suspension indefinitely. To obtain a measure of the relative amount in each classification the Michigan Water Resources Commission developed an "unsettleable suspended solids" test. In this test a 500 ml graduate is filled with the sample and allowed to stand quiescent for a period of two hours. A 400 ml portion of the supernatant is then decanted or siphoned off and a standard suspended solids test made on it. This suspended material is referred to as unsettleable suspended solids.

Suspended solids may settle in and obstruct navigation channels, ditches or conduits. They cause the water to be turbid and unsightly. This is particularly true for the finer less settleable solids which may remain in suspension until the stream water reaches a lake or ocean. Blankets of solids on stream or lake beds may destroy aquatic bottom-life so that fish dependent on these organisms are reduced. Increased suspended solids in a water to be filtered for domestic or industrial supplies may necessitate use of more flocculating chemicals, decrease filter runs, and increase sludge accumulation.

References: For suspended solids, Tenth Edition, Standard Methods for the Examination of Water and Sewage.
For unsettleable suspended solids, Michigan Water Resources Commission.

h. Iron

Determinations were made for both total and dissolved iron. The samples for dissolved iron analysis were filtered and the analysis run on the filtrate. The dissolved iron is the soluble portion which is present in the form of ferrous sulphate from pickling. The difference between the two values is suspended iron due to mill scale.

Iron is objectionable in water supplies used for both domestic and industrial purposes. The Public Health Service Standards for Drinking Water state that the iron and manganese together should not exceed 0.3 ppm. Iron and iron compounds may cause tastes and odors in drinking water and will stain plumbing fixtures and laundered materials. Manufacturing processes may require low concentration or absence of iron.

Reference: Standard Methods for the Examination of Water and Sewage, Tenth Edition. American Public Health Association.

i. Alkalinity, Acidity and pH

Alkalinity of water is usually due to carbonates, bicarbonates and hydroxides, and less frequently borates, silicates, and phosphates. The acidity of a water is usually due to mineral acids, salts of strong acids and weak bases, and uncombined carbon dioxide. The acid and alkaline constituents interact to neutralize each other. The relative abundance of either group de-

termines the hydrogen ion concentration of the water (pH). Thus the acidity of spent pickle liquor will be partially neutralized and the pH increased by alkalinity of other wastes or water with which it mixes. Water with pH in either the upper or lower extremes may be toxic to aquatic life and may be corrosive or more expensive to treat for industrial or domestic uses.

The amount of alkalinity is determined by titration with a standard solution of acid to certain hydrogen ion concentrations as determined by indicator solutions or a pH meter. Thus the titer necessary to reduce the pH to 8.3 (the color change point of phenolphthalein) is referred to as phenolphthalein alkalinity, and the titer necessary to reduce the pH to 4.5 (the color change point of methyl orange) is called total alkalinity. The amount of acidity is determined by titration with a standard solution of a base to the same hydrogen ion concentrations used to measure alkalinity. Thus the titer necessary to raise the pH to 4.5 is called mineral acid acidity and the titer necessary to raise the pH to 8.3 is called the total acidity. The acidity or alkalinity results are expressed as parts per million of calcium carbonate ($CaCO_3$).

Reference: Standard Methods for the Examination of Water and Sewage, Tenth Edition, American Public Health Association.

APPENDIX C

RELATIONSHIP BETWEEN CONTAMINANTS IN COKE QUENCHING WATER AND IN BLAST FURNACE GAS WASH WATER

	Page
INTRODUCTION	58
GENERAL INFORMATION	58
1. Purpose	59
2. Dates	59
MANUFACTURING PROCESS	59
3. Coke and By-Product Plant	59
4. Quenching System	59
5. Blast Furnace and Blast Furnace Gas Washing Facilities	63
PROCEDURES OF STUDY	64
6. Sampling Method	64
7. Preservation of Samples	66
8. Flow Measurements	66
9. Analysis Performed, Significance, and Method	68
PRESENTATION AND DISCUSSION	69
10. Phenol Carryover	69
11. Carryover of Ammonia and Cyanides	77

INTRODUCTION

The fact that blast furnace gas wash water in some instances contained significant concentrations of phenols was uncovered in industrial waste surveys in 1951 (1). Information obtained in 1954 in a special survey reinforced the suspicion that the use of waters containing phenols for quenching coke resulted in a carryover of phenols on the coke to the blast furnace where they volatilize and subsequently contaminate the blast furnace gas wash water (2).

It is probable that such carryover could be reduced by dephenolization of the ammonia still wastes prior to their use for quenching coke. The Great Lakes Steel Company's new coke plant and blast furnace on Zug Island in Detroit, Michigan, incorporated a dephenolization system and a closed recirculated quenching system using ammonia still waste and other contaminated coke plant wastes. The facilities of the Great Lakes Steel Company offered opportunity to determine the carryover of phenols with ammonia still wastes (1) partially dephenolized, (2) efficiently dephenolized, and (3) undephenolized. This report contains the details and findings of such a study.

The ultimate question this study was intended to answer is whether or not dephenolization is justified where the wastes are used to quench coke. Air pollution as well as water pollution considerations are involved. Unfortunately time and facilities available did not permit

sampling or analysis of vapors or gases emanating from the quench station.

Use of ammonia still and other by-product coke plant wastes in a closed system for quenching coke is an effective method of waste control for stream protection. In pointing out the carryover of phenols by this operation it is not intended to question the advantages of this disposal method.

1. Purpose

The study was for the purpose of determining the relationship between phenols in waste waters used for quenching coke and in blast furnace gas wash water waste. A secondary objective was to determine the relationship of cyanides, thiocyanates, and ammonia in these wastes.

2. Dates

Dates on which samples of the water used for coke quenching and blast furnace gas wash water were collected were as follows:

March 28, 1955 through March 30, 1955

April 3, 1955 through April 7, 1955

May 2, 1955 through May 6, 1955 and May 24, and 25, 1955

MANUFACTURING PROCESS

3. Coke and By-Product Plant

The coking process and by-product recovery plant have been described in the main body of the report.

4. Quenching System

The sources of water used for coke quenching and the coke quenching

water supply system as operated during the test are shown diagramatically in Figure 10.

Limited time and personnel did not permit special study of all three quench stations and the gas wash water waste from all three furnaces. The new quench station, serving blast furnace D was selected as most suitable for the work.

The entire flow of contaminated wastes from the No. 2 coke plant was pumped to the new quench station. The wastes were supplied to the basin through a float controlled valve in a stilling basin adjoining the quench water settling basin. The quantity of wastes was greater than needed at this one quench station. The excess was wasted to the sewer through a hose which was attached to a connection in the supply line to the basin.

At times the pumping rate to the quench sprays was greater than the waste supply to the station. A float operated valve admitted fresh water to the pump at these times. If the water level in the waste collecting sump which supplied the pump dropped below a set level fresh water was admitted. Operators were instructed to regulate the valve which permitted the wastes to flow to the quench station so that the water level in the waste collecting sump, from which the quench station was supplied, remained above that at which fresh water was automatically added. This was undertaken to assure quench water of uniform quality. Occasionally insufficient attention was devoted to this detail and dilution water was not excluded all of the time.

When a quench car receives a hot load of coke from the coke oven it is driven into the quench station. The sprays are turned on and automatically operate for a set time; during the survey this time limit was set at two

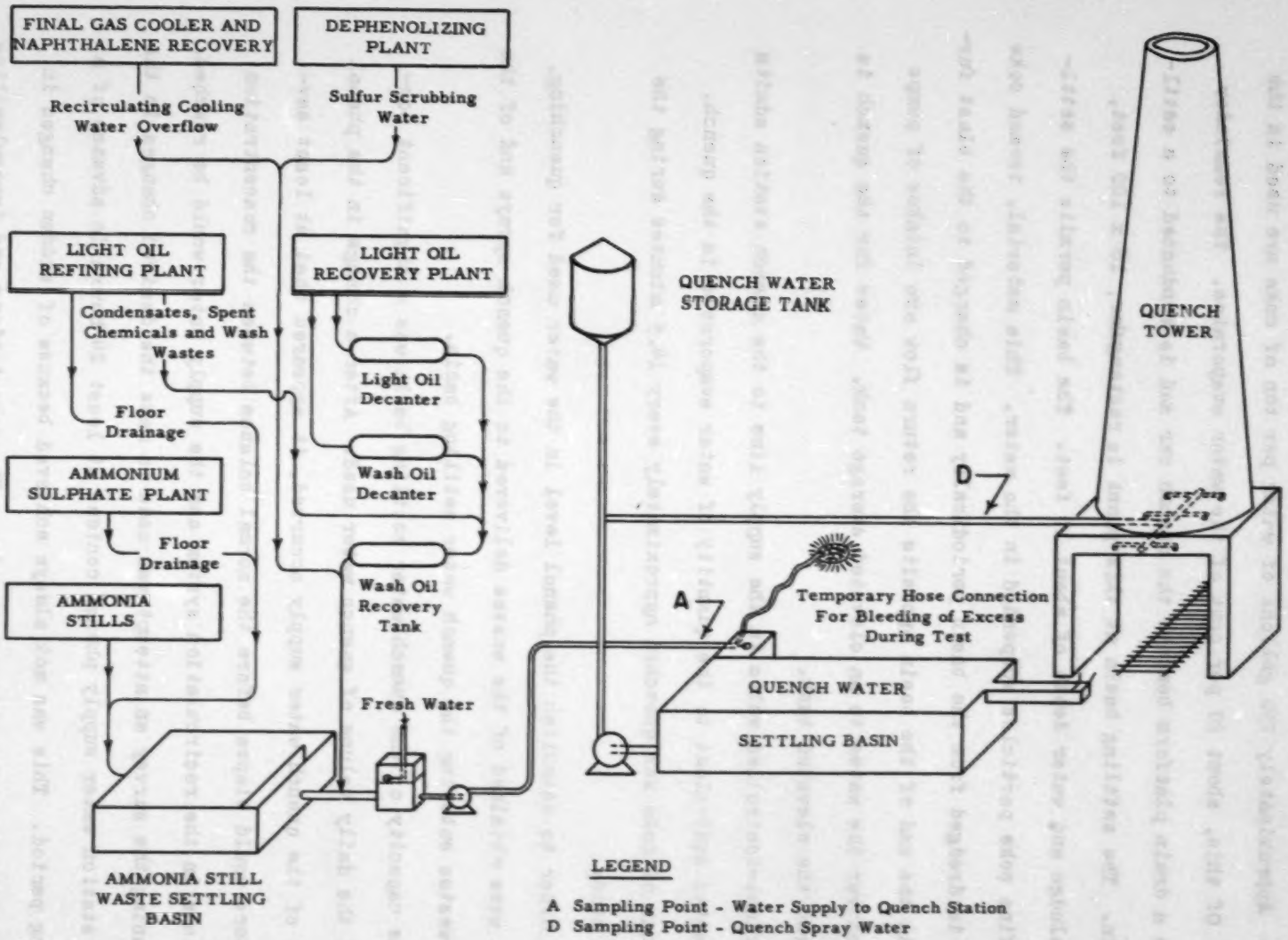


FIGURE IC COKE QUENCHING SYSTEM USED FOR TESTS ON CARRY-OVER

minutes. Approximately 750 gallons of water per ton of coke are used in the quench. Of this, about 20 per cent of the water evaporates. The remainder falls to a drain platform beneath the quench car and is conducted to a settling basin. The settling basin at this plant is rectangular, 16 x 100 feet, with a sludge and water depth of about 10 feet. The basin permits the settling of fine coke particles suspended in the water. This material, termed coke breeze, is dredged from the basin periodically and is charged to the blast furnace. At the end of the basin opposite the return flow are intakes of pumps which deliver the water to an elevated storage tank. Water for the quench is drawn from the elevated tank.

A float-controlled valve in the supply line to the quench station admits fresh wastes equivalent to the quantity of water evaporated in the quench.

A car of coke was quenched approximately every 14.5 minutes during the special study.

In order to establish the phenol level in the water used for quenching, samples were obtained of the wastes delivered to the quench sprays and of the makeup wastes entering the quench water settling basin.

The capacity of the quench water settling basin was a significant portion of the daily volume of quench water used. After a change in the phenol content of the quench water supply occurred, it appeared that at least several hours would elapse before the normal balance between the concentration of phenols in the recirculation system and the supply water would be reached. In planning the survey an attempt was made to make the desired changes in the quench station water supply phenol content at least 24 hours in advance of a sampling period. This was not always achieved because of sudden changes in ammonia still or dephenolizer operation. These variations and irregularities

were to be expected in breaking in a new plant.

It should be noted that nearly all of the ammonia still and concentrated coke plant wastes from all of the coke produced were being pumped to one quench station where a portion of the wastes were used to quench coke. Therefore the phenol concentrations in the quench water were higher than normally would exist in a quenching system in which the total coke plant wastes were used to quench the total quantity of coke, and fresh water makeup would be necessary.

Blast Furnace D used exclusively coke quenched at the new quench station. Each carload of quenched coke is left in the quench station for several minutes after the quench water sprays are cut off to allow water to drain from the coke. The quench car then moves to a hopper into which the coke is dumped. Any remaining coke which still has a tendency to burn is water quenched in the hopper by a hand directed hose. From the dump hopper it is fed by hand operated gates in an even stream to a belt conveyor. The conveyer carries the coke to a hopper supplying the skip hoists of the blast furnace. Usually three quench car dumps are accumulated in the hopper before the conveyor is started and coke delivered to the furnace. The average lapse between the time the coke is quenched and the time it enters the blast furnace is estimated as 45 minutes.

The water used to hose down coke in the car dumping hopper and any residual drainage from the quenched coke drains to a sump in the hopper. It is pumped to the plant sewers where it joins the wastes going to the river.

5. Blast Furnace and Blast Furnace Gas Washing Operations

Blast Furnace D is a new furnace which was placed in operation in January,

1955. The furnace was constructed for pressure operation and at the time of the tests was operated at about 6.5 psi top pressure. The pressure regulating valve is located between the gas washer and the electrical precipitator.

A factor in operation of this furnace is the use of a considerable portion of scrap iron in the charge. This results in an unusually low use of coke per ton of pig iron produced.

The blast furnace primary gas washer is a spiral tile packed tower which uses a large volume of wash water.

The final gas cleaning is accomplished by two plate electrical precipitators. The precipitators are irrigated by a continuous flow of about 400-450 gpm each and three times per day are flushed for half hour periods with a flow of about 650 gpm each.

A small stream of water, estimated at 25 gpm, is sprayed onto the pressure regulating valve to keep it flushed clean. The water also picks up considerable dust from the gases.

The primary gas washer effluent, electrical precipitator irrigation and flushing water, and flushing water from the pressure regulating valve combine in a sump from which they are pumped to clarifiers. The combined wastes as they were pumped to the clarifiers were sampled for purposes of this study. The fresh water supply to the gas washers was also sampled.

PROCEDURES OF THE STUDY

6. Sampling Method

Samples were routinely collected from the following points:

Point	Designation
Waste water supply to the Quench Station	A
Quench Spray	D
Water Supply to Gas Washers	C
Blast Furnace Gas Wash Water Waste	B

The sampling points at the quench station are indicated on Figure 10.

Each daily sample was collected and composited over approximately eight hour periods beginning about 8:00 A.M.

The waste water supply to the quench station was sampled on March 28 and 29 by collecting and compositing equal quantities of the wastes at half hour intervals. Beginning with the March 30 sample a device was installed for collecting a small portion of the waste continuously. At half hour intervals equal portions of the continuously collected sample were added to a compositing vessel.

The water flowing to the quench spray was sampled continuously during each quench in the early part of the survey. In the latter part samples were collected during every other quench.

Samples of the water supply to the gas washers were obtained by dipping equal quantities from the supply conduit at half hour intervals.

Blast furnace gas wash water wastes were sampled from a drain valve on the line supplying the pumps which delivered the wastes to the Thickeners.

Special composite samples were collected from the dephenolizing plant feed and effluent, ammonia still feed and waste, the light oil condensate, and the final cooler recirculation system overflow. Analysis of these samples supplied information on the source of phenols and the efficiency of the dephenolizer.

7. Preservation of Samples

Samples for analyses for phenols, cyanides and thiocyanates were preserved by the addition of caustic soda to the compositing bottle to maintain a pH of above 10. The composites were checked frequently and additional caustic added if necessary.

Samples for ammonia analyses were preserved by adding sulfuric acid to the compositing bottle to maintain the pH below 4.

8. Flow Measurement

The quantity of makeup water fed to the new coke quenching station is equal to the amount of water evaporated on the coke plus that remaining on the quenched coke. Measurements were made of the quantity of water evaporated and entrained with quench-carloads of coke. These measurements were made by closing off the quench station supply and measuring the drop in water level in the quench water settling basin after a quench was completed. The water levels were read to thousandths of a foot using a hook gage and are considered accurate to within 5 per cent. The quantity of coal charged to each oven is known fairly accurately and the yield is determined each day. These data provided a basis for computing tons of coke per quench load and the gallons of water separated per ton of coke. The data are tabulated below:

Date Month 1955	Time	Volume Used from Quench Basin	Quantity of Coke Quenched Tons	Volume of Water Evaporated and Entrained per Ton of Coke Quenched Gallons
March 25	4:30 PM	2140	13.1	163
	10:37 AM	2090	13.1	160
March 30	10:51 AM	1890	13.1	144
	3:42 PM	1970	13.1	150
	3:52 PM	3980	26.2	152
TOTALS		12070	78.6 Avg.	153

The amount of coke quenched during the test periods was obtained from plant records. The total volume of makeup water to the quench station was computed from the average 153 gallons of water evaporated and entrained per ton of coke and the coke production data.

The quantity of water actually applied to the coke through the sprays is several times greater than the makeup because the water is recirculated. The volume of quench spray water was computed from the volume of quench station supply by assuming that 20 per cent of the water applied to the coke was evaporated.

The dephenolizer plant and ammonia still weak liquor feed rates were measured by orifice meters and recorders with which these units were equipped. Ammonia still waste was estimated from the weak liquor feed rates, plant recorder records of steam applied to the stills, and rotometer readings of makeup water used in the lime slurry. Light oil condensate waste was measured by timing the filling of a container of known volume. Final cooler water overflow was measured by closing off the overflow pipe of the basin and measuring

the rise in water level during a measured time interval. Overflow from the quench system was measured by determining the time required to fill a container of known volume.

The volume of gas wash water is measured by an orifice meter and recorded automatically. The lines to the measuring and recording device were flushed out and the instrument checked and zeroed at the beginning of the study.

The irrigator spray water was measured by non-recording orifice meter. This meter was read three times during each sampling shift.

9. Analyses Performed, Significance and Method

The methods and meanings of analyses performed on the samples are discussed in Appendix B of this report. Phenols were of primary interest, and ammonia and cyanide of secondary interest. Thiocyanate analyses were made in order to trace possible conversion of the cyanides to thiocyanates in the system.

Experiments were carried out to determine what steps were necessary to remove interfering substances preliminary to phenol analysis. Results of these tests are given below.

		Screening Procedure	
Source of Sample	Sample Date	Single Distillation Phenols ppm	Complete Screening (Distillation, Chloroform Extration, Salting Out, Caustic Extraction, and Distillation) Phenols ppm
Quench Station Water Supply	March 19	110	105
Quench Station Spray	March 29	60	59
Blast Furnace Gas Wash Water Waste	March 29	0.89	0.49*
	April 4	1.3	1.1
	April 5	1.2	1.1
	April 7	0.94	0.64

* Considered in error by analyst due to lab accident.

It was decided that simple distillation was sufficient treatment for removing interfering substances prior to phenol analysis.

PRESENTATION AND DISCUSSION OF DATA

Individual analytical results and flow data obtained during the survey are given in Table C3, which appears at the end of Appendix C.

10. Phenol Carryover

The relationship between constituents in quench station water supply and quench station spray is an important factor in evaluating the findings on phenol carryover. If the concentration of a constituent in the quench station supply were held constant for a considerable period it appears that the concentration in the quench spray should become constant. A change in the concentration of the constituent in the quench station supply would be expected to result in a new level of the constituent in the spray water. It is probable that at least several hours were required for establishment of a constant relationship between concentrations in the supply and the spray water because of the large volume of the quench system. Many changes in the concentration of constituents in the quench station supply occurred during this study. Some were made intentionally, while others were unavoidable in operation of a new coke plant. A normal relationship should prevail in the quench system to assure a normal relationship between quench station supply and blast furnace gas wash water.

Data on the relationships between concentration of constituents in the quench station supply and quench station spray water are tabulated in Table C3. The data for phenols are plotted in Figure 2C. A linear relationship is indicated by the plot for phenols. Data for thiocyanates also show a definite linear relationship. Inspection of the supply and spray water concen-

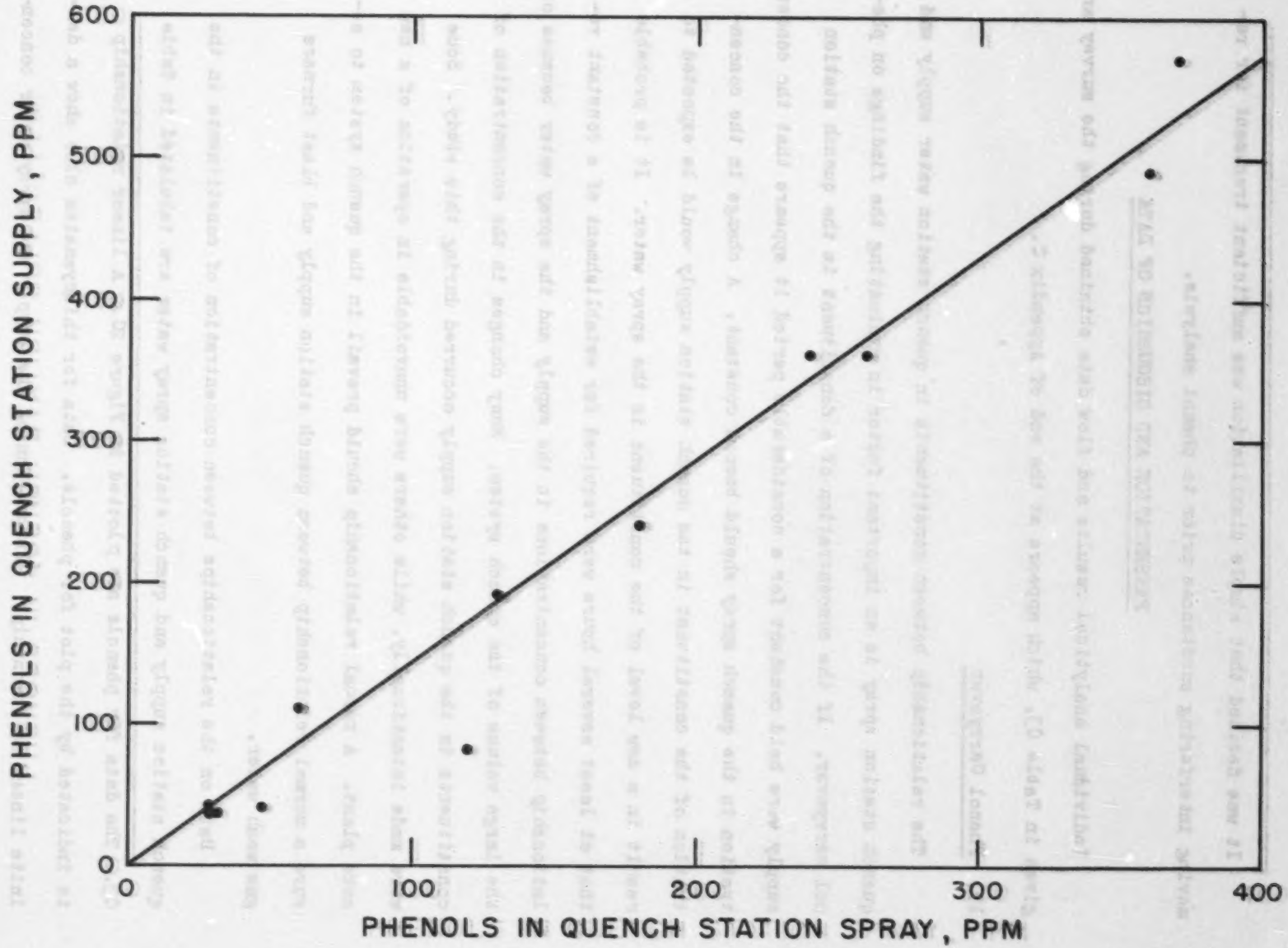

PHENOLS IN QUENCH STATION SUPPLY, PPM
600
500
400
300
200
100
0
0
100
200
300
400
PHENOLS IN QUENCH STATION SPRAY, PPM

FIGURE 2C

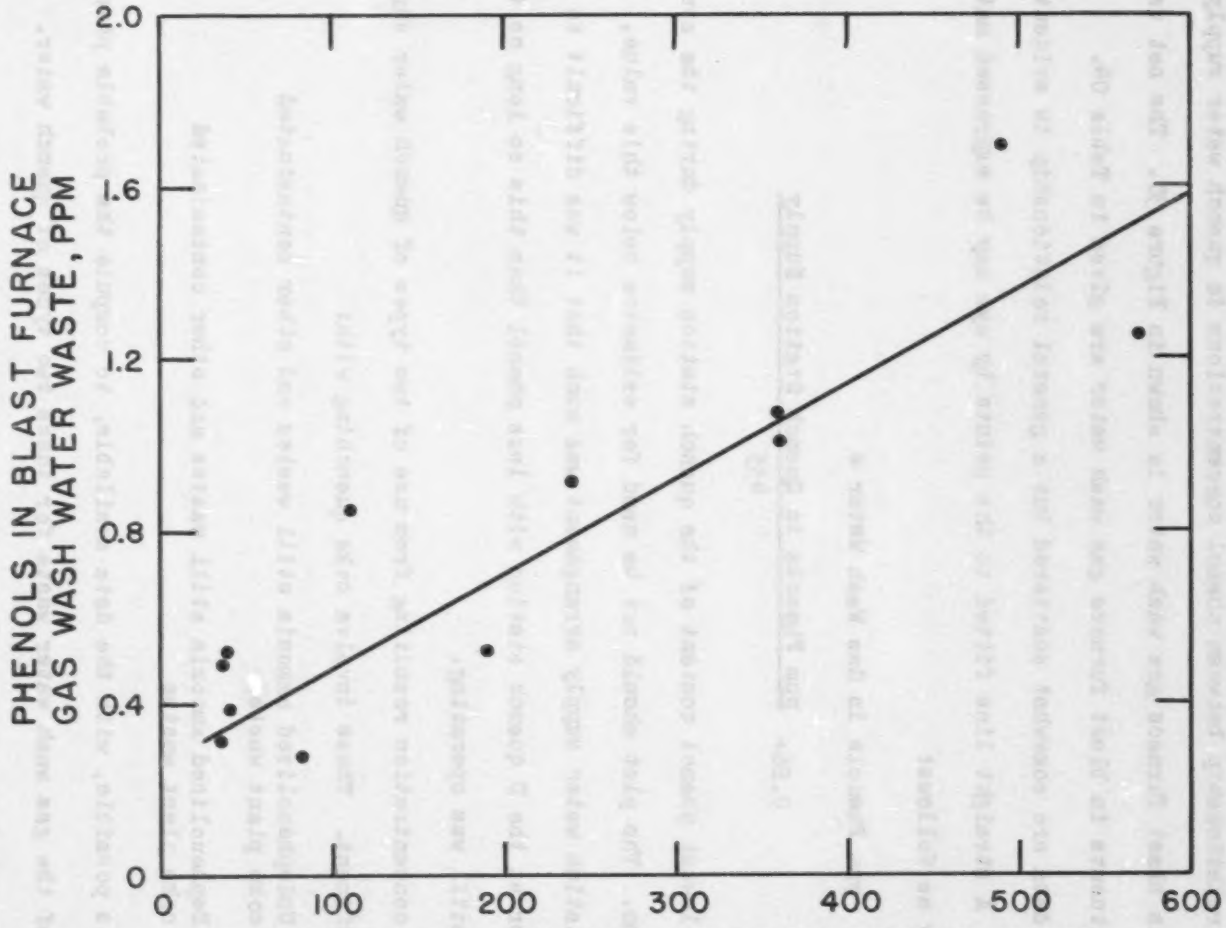

PHENOLS IN BLAST FURNACE GAS WASH WATER WASTE, PPM
2.0
1.6
1.2
0.8
0.4
0
0
100
200
300
400
500
600
PHENOLS IN QUENCH STATION SUPPLY, PPM

FIGURE 3C

trations indicate that changes in quality of the supply water were reflected in the spray water for most samples.

The relationship between phenol concentrations in quench water supply and phenols in blast furnace gas wash water is shown in Figure 3C. The net values of constituents in blast furnace gas wash water are given in Table C4.

The data are somewhat scattered but a general relationship is evident for phenols. A straight line fitted to the points by eye may be expressed mathematically as follows:

$$\text{ppm Phenols in Gas Wash Water} = 0.26 + \frac{\text{ppm Phenols in Quench Station Supply}}{455}$$

The lowest phenol content of the quench station supply during the study was 35 ppm. The plot should not be used for estimates below this value. The quench station water supply arrangement was such that it was difficult to obtain water at the D quench station with less phenol than this so long as the ammonia still was operating.

The concentration resulting from use of two types of quench water supply are significant. These involve coke quenching with:

1. Undephenolized ammonia still wastes and other contaminated coke plant wastes
2. Dephenolized ammonia still wastes and other contaminated coke plant wastes

It is possible, with the data available, to compute the probable phenol content of the gas wash water waste for these two types of quench water.

There are four sources of phenols in the quench water system.

(1) The raw ammonia liquor fed to the dephenolizer contained an average

of about 1550 pounds of phenols per day (Table C6). This is in fair agreement with plant records, which indicated about 1700 pounds per day in the ammoniacal liquor. Without dephenolization it may be assumed that about 70 to 80 per cent of the phenols would be present in the ammonia still wastes. The other 20 to 30 per cent would be volatilized and returned to the gas stream. This portion of the phenols should be present in subsequent wastes such as final cooler overflow and benzol plant wastes. Therefore it is assumed that without dephenolization all of the phenols in the raw ammonia liquor (1550 pounds) would be present in the coke plant wastes used for quenching.

(2) The final gas coolers remove some residue phenols from the gas. These phenols enter the quench water system through the overflow from the final cooler recirculation system. One measurement of the volume and concentration of the final cooler overflow, with the dephenolizer operating, showed that the overflow contained 108 pounds per day of phenols.

(3) Some phenols are removed by the light oil scrubbers and enter the liquid wastes of the stripping and light oil fractionating operations. The data in Table C6 indicates this waste carries about 10 pounds per day of phenols.

(4) As explained in the main text of the report another source of phenol bearing wastes is the ammonia concentrator wastes from the No.1 cokeplant. The company reported this waste to contain about 180 pounds of phenols per day. There are also some phenol bearing wastes from the light oil recovery operations in the No.1 coke plant. The phenols in these light oil wastes are assumed to be negligible and are neglected in subsequent computations.

A summary of phenols from these sources is:

Phenols in Ammoniacal Liquor	1550 lbs/day
Phenols in Final Cooler Overflow	108 lbs/day
Phenols in Benzol Plant Wastes	10 lbs/day
Phenols in Ammonia Concentrator Wastes from Plant No. 1	180 lbs/day
Total	1,848 lbs/day

The volume of quench water in which this quantity of phenols occurs is:

Coke Produced Per day	4,800 Tons
Gallons Quench Water Per Ton of Coke	153 Gal.
Total Quench Water Supply (4,800x153)	735,000 Gal.

On the basis of the above data the concentration of phenols in quench water without dephenolization would be 302 ppm.

The efficiency of the dephenolizer was found to be 95.5 per cent (Table C6). With the dephenolizer in operation 4.5 per cent of the phenols in the weak ammonia liquor, or 70 pounds, would remain in the feed to the ammonia still. As explained previously, most of the 70 pounds will go into the ammonia still wastes, but a fraction may carry through into other coke plant wastes. The total quantity in the wastes would be:

Ammonia Still Wastes	70 lbs/day
Phenols in Final Cooler Overflow	108 lbs/day
Phenols in Benzol Plant Wastes	10 lbs/day
Phenols in Ammonia Concentrator Wastes from Plant No. 1	180 lbs/day
Total	368 lbs/day

This amounts to an estimated concentration of 60 ppm in the quench water system.

The estimates in Table C1, are based on the above estimated concentrations of phenols in the quench water system and the relation between phenols in the system and in the blast furnace gas wash water waste (Fig. 36). The total gas wash water waste value was computed from the data on wash water waste flow from Furnace D and total coke production for the entire plant.

TABLE C1

ESTIMATED PHENOLS IN BLAST FURNACE GAS WASH WATER

Source of Water or Wastes Used in Quenching	Phenols in Water Wastes Used for Quenching ppm	Phenols in Blast Furnace Gas Wash Water Wastes: Concentration ppm	Quantity in Total Gas Wash Water Wastes from Plant lbs.	Quantity Per Ton of Pig Iron Produced lbs.
Total Coke Plant Wastes with Dephenolizer Operating	60	0.39	48	0.0108
Total Coke Plant Wastes with Dephenolizer Not Operating	302	0.92	113	0.0256

Table C1 covers estimated phenols potentially present in blast furnace gas wash water wastes only. It does not deal with total phenols discharged to the river by various combinations of plant operation.

The estimated loads on the river with different systems of quenching and dephenolizing are given in Table C2.

TABLE C2

PHENOL LOADS TO RIVER WITH DIFFERENT QUENCHING AND DEPHENOLIZATION ARRANGEMENTS

Quench Water Supply	Wastes to River	Phenols to River in Blast Furnace Gas Wash Water and Coke Plant Wastes, lbs.
Fresh Water	Blast Furnace Gas Wash Water, Dephenolized Ammonia Liquor, Ammonia Concentrator Wastes, Other Coke Plant Wastes	368
Coke Plant Wastes Dephenolizer Operating	Blast Furnace Gas Wash Water	48
Coke Plant Wastes Without Dephenolizer Operating	Blast Furnace Gas Wash Water	113

These data indicate that, when quenching with total coke plant wastes, operation of the dephenolizer would reduce the phenols entering the river from 113 to 48 pounds per day, or 65 pounds daily.

They indicate that quenching with undephenolized wastes would reduce this phenol load from 368 pounds per day, for fresh water quenching and dephenolizing of ammoniacal liquor, to 113 pounds per day, or 255 pounds daily.

The phenol load of 108 pounds per day in the final cooler overflow is an important factor in the total discharge to the river. At some plants evaporation exceeds condensation in the final cooler system and no overflow occurs. The overflow in this plant results from the addition of sulfur scrubbing water from the phenol recovery plant and fresh water to the final cooler water system. If overflow from this system were eliminated, the phenol load with dephenolization and fresh water quenching would be close to that of 113 pounds per day for quenching with undephenolized wastes.

11. Carryover of Ammonia and Cyanides

Inspection of the data indicates there was no correlation between the ammonia and cyanides in the quench water and in the gas wash water wastes.

TABLE 03

GROSS CONCENTRATIONS IN QUENCH WATER, GAS WASH WATER, AND COKE PLANT WASTES

Date of Sample	Source of Sample	Phenols ppm	Ammonia (as N) ppm	Cyanides (as CN) ppm	Thiocyanates (as CN) ppm	Flow MGD
3/28/55	Plant #2 Quench	110	1,820	31.4	140	0.210
3/29/55	Station Water	190	1,520	68.4	270	0.211
3/30/55	Supply (A)	360	1,670	99.0	230	0.211
4/3/55		570	350	40.8	150	0.211
4/4/55		490	672	28.2	160	0.210
4/5/55		82	-	-	-	0.210
4/7/55		360	1,040	13.8	91	0.211
5/2/55		40	298	10.6	58	0.222
5/3/55		37	2,430	29.8	170	0.212
5/4/55		35	458	26.3	200	0.222
5/5/55		35	136	31.9	210	0.215
5/6/55		240	108	36.4	170	0.225
5/25/55		37.9	1,860	-	-	0.216
3/28/55	Plant #2 Quench	60	1,620	28.2	170	0.210
3/29/55	Station Spray	130	2,730	146	360	0.211
3/30/55	(D)	240	2,550	27.8	330	0.211
4/3/55		370	1,240	11.7	250	0.211
4/4/55		360	840	10.5	250	0.210
4/5/55		120	-	-	-	0.210
4/7/55		260	1,700	7.70	190	0.211
5/2/55		47	218	10.6	160	0.222
5/3/55		29	1,760	15.0	220	0.212
5/4/55		30	748	8.30	280	0.222
5/5/55		29	162	17.2	280	0.215
5/6/55		180	52.5	24.8	220	0.225
3/28/55	D Blast Furnace	0.89	6.0	0.52	0.77	5.20
3/29/55	Gas Wash Water	0.56	4.8	0.63	1.10	5.50
3/30/55	Waste (B)	1.10	2.4	1.25	2.30	5.01
4/3/55		1.30	9.4	0.54	1.50	5.01
4/4/55		1.70	5.5	0.37	1.30	5.31
4/5/55		0.29	-	-	-	5.16
4/7/55		0.94	8.4	0.47	0.63	5.31
5/2/55		0.83	5.8	0.58	1.60	5.31
5/3/55		0.52	7.6	1.02	1.90	5.33
5/4/55		0.34	11.0	0.71	1.60	5.37
5/5/55		0.50	4.8	1.28	2.30	5.28
5/6/55		0.92	4.7	0.80	1.50	5.33

Great Lakes Steel Corporation
Continued

Date of Sample	Source of Sample	Phenols ppm	Ammonia (as N) ppm	Cyanides (as CN) ppm	Thiocyanates (as CN) ppm	Flow MGD
3/28/55	Mill Water Supply	0.036	0.02	0.021	0.013	-
3/29/55	(C)	0.039	0.05	0.003	0.018	-
3/30/55		0.039	0.0	0.180	0.019	-
4/3/55		0.052	0.27	0.090	0.016	-
4/4/55		0.024	0.93	0.087	0.0	-
4/5/55		0.021	-	-	-	-
4/7/55		0.036	0.23	0.052	0.012	-
5/1/55		0.022	0.52	0.027	0.020	-
5/2/55		0.450	0.43	0.017	0.020	-
5/3/55		0.009	0.79	0.039	0.0	-
5/4/55		0.026	0.78	0.031	0.050	-
5/5/55		0.012	1.00	0.053	0.009	-
5/6/55		0.011	0.51	0.005	0.009	-
3/30/55	Dephenolization	990	9,870	490	980	0.195
5/24/55	Plant Feed (E)	770	-	-	-	0.223
5/25/55		650	-	-	-	0.228
3/30/55	Dephenolization	990	8,660	372	830	0.195
5/24/55	Plant Effluent	35.7	-	-	-	0.223
5/25/55	(F)	28.8	-	-	-	0.228
3/30/55	Ammonia Still	750	9,640	410	940	0.260
5/25/55	Feed (J)	35.9	11,900	-	-	0.234
3/30/55	Ammonia Still	480	1,790	39	240	0.349
5/25/55	Waste (G)	22.3	2,620	81.2	-	0.311
3/30/55	Light Oil Con-	32	-	18.5	31	-
5/25/55	densate (H)	40.2	-	24.5	26.6	0.033
5/25/55	Final Cooler Water	211	-	210	273	0.061

TABLE C4

NET CONCENTRATIONS IN GAS WASH WATER

(Concentrations of Pollutants in Water Supply Subtracted)

Date of Sample	Source of Sample	Phenols ppm	Ammonia (as N) ppm	Cyanides (as CN) ppm	Thio-cyanates (as CN) ppm	Flow MGD
3/28/55	D Blast Furnace Gas Washer Water Waste	0.85	6.0	0.50	0.76	5.20
3/29/55		0.52	4.8	0.63	1.08	5.50
3/30/55		1.06	2.4	1.07	2.28	5.01
4/3/55		1.25	9.1	0.45	1.48	5.01
4/4/55		1.68	4.6	0.28	1.30	5.31
4/5/55		0.27	-	-	-	5.16
4/7/55		0.90	8.2	0.42	0.62	5.31
5/2/55		0.38	5.4	0.56	1.58	5.31
5/3/55		0.51	6.8	0.98	1.90	5.33
5/4/55		0.31	10.2	0.68	1.55	5.37
5/5/55		0.49	3.8	1.23	2.29	5.28
5/6/55		0.91	4.2	0.80	1.49	5.33

Correction to net concentrations is not appropriate to other samples, net concentrations are same as gross.

TABLE C5

VOLUME OF GAS WASH WATER PER TON OF PIG IRON PRODUCED

Date	D Furnace Pig Iron Production Tons	Flow Gas Wash Water Waste M.G.D.	Volume Gas Wash Water Wastes Per Ton of Pig Iron Produced Gallons
3/28/55	1440	5.20	3610
3/29/55	1612	5.50	3410
3/30/55	1700	5.01	2950
4/3/55	1701	5.01	2950
4/4/55	1842	5.31	2890
4/5/55	1572	5.16	3290
5/2/55	1720	5.31	3090
5/3/55	1690	5.33	3150
5/4/55	1713	5.37	3140
5/3/55	1752	5.28	3010
5/6/55	1530	5.33	3480
		Average	3180

TABLE C6

QUANTITY OF POLLUTANTS IN PROCESS STREAMS AND WASTES OF COKE PLANT

Date of Sample	Source of Sample	Phenols lbs/day	Ammonia (as N) lbs/day	Cyanides (as N) lbs/day	Thiocyanates (as CN) lbs/day	Flow MGD
3/30/55	Dephenolization Plant Feed (E)	1610	16,000	795	1590	0.195
5/24/55		1430	-	-	-	0.223
5/25/55		1235	-	-	-	0.228
3/30/55	Dephenolization Plant Effluent (F)	1610	14,000	605	1350	0.195
5/24/55		66	-	-	-	0.223
5/25/55		55	-	-	-	0.228
3/30/55	Ammonia Still Feed (J)	1630	20,900	890	2040	0.260
5/25/55		70	23,200	-	-	0.234
3/30/55	Ammonia Still Wastes (G)	1400	5,210	113	698	0.349
5/25/55		58	6,800	211	-	0.311
3/30/55	Light Oil Condensate (H)	8.8	-	5.1	8.5	(0.033)
5/25/55		11.1	-	6.7	7.3	0.033
5/25/55	Final Cooler Water	108	-	107	139	0.061

	Efficiency of Dephenolizer Per Cent Reduction in Phenols
3/30/55	0
5/24/55	95.4
5/25/55	95.5

	Efficiency of Ammonia Still Per Cent Reduction in Ammonia
3/30/55	75.1
5/25/55	70.7

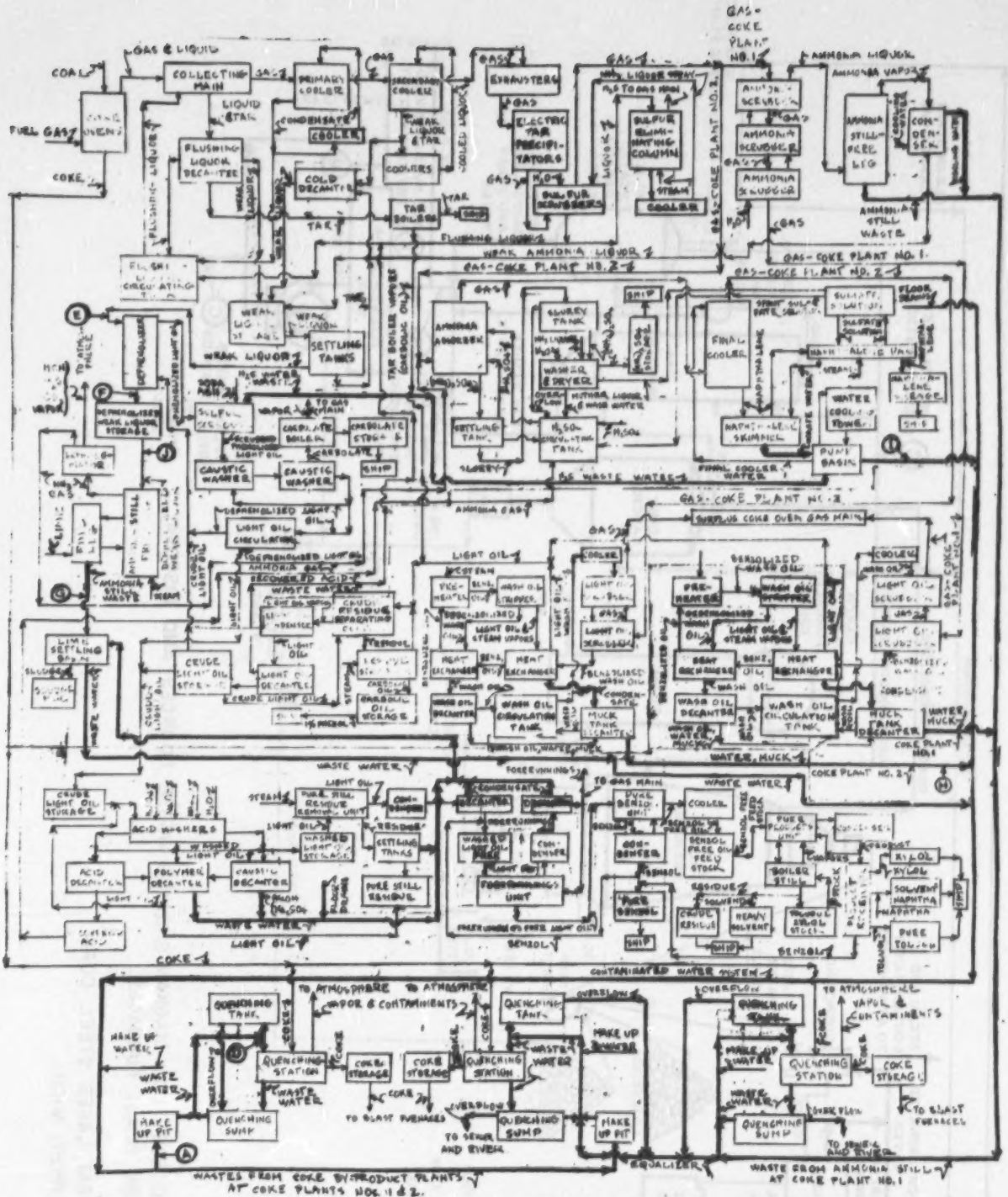
REFERENCES FOR APPENDIX C

1. Unpublished Report. Industrial Wastes Section, Environmental Health Center, Public Health Service, Cincinnati, Ohio, May 1951.

2. Black, H. H., and McDermott, G. N., "Industrial Waste Guide, Blast Furnace Department of the Steel Industry," Sewage and Industrial Wastes, 26, 8, 967 (August 1954).

APPENDIX D

PROCESS FLOW DIAGRAMS



LEGEND:

- (A) → SAMPLING STATION
- —— PROCESS FLOW LINE
- ═══ WASTE FLOW LINE

NOTES:
THERE ARE TWO COKE PLANTS WITH DUPLICATE PROCESSES FROM THE COKE OVENS THROUGH THE SULFUR ELIMINATING COLUMNS. BOTH PLANTS ARE DIAGRAMMED AS ONE UP TO THE POINT OF AMMONIA REMOVAL FROM THE GAS STREAMS.
COKE PLANT NO. 1 - 1,400 TONS/DAY COAL
COKE PLANT NO. 2 - 1,100 TONS/DAY COAL

FIGURE NO. 1

FLOW DIAGRAM
COKE BY-PRODUCTS PLANTS AND COKE QUENCHING

GREAT LAKES STEEL CORP.
BLAST FURNACE DIVISION

DETROIT, MICH.

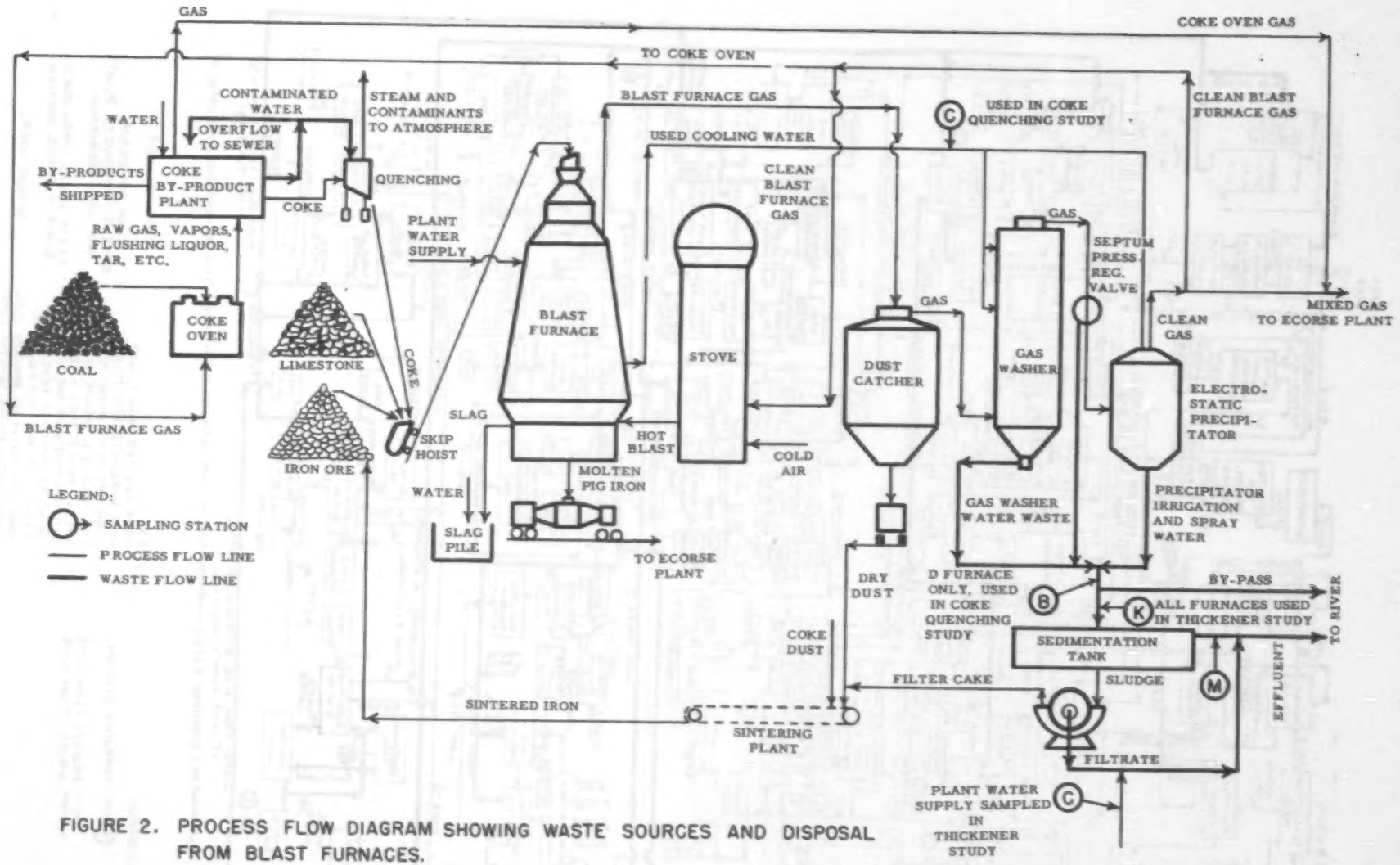


FIGURE 2. PROCESS FLOW DIAGRAM SHOWING WASTE SOURCES AND DISPOSAL FROM BLAST FURNACES.

GREAT LAKES STEEL CORP.
DETROIT, MICH.

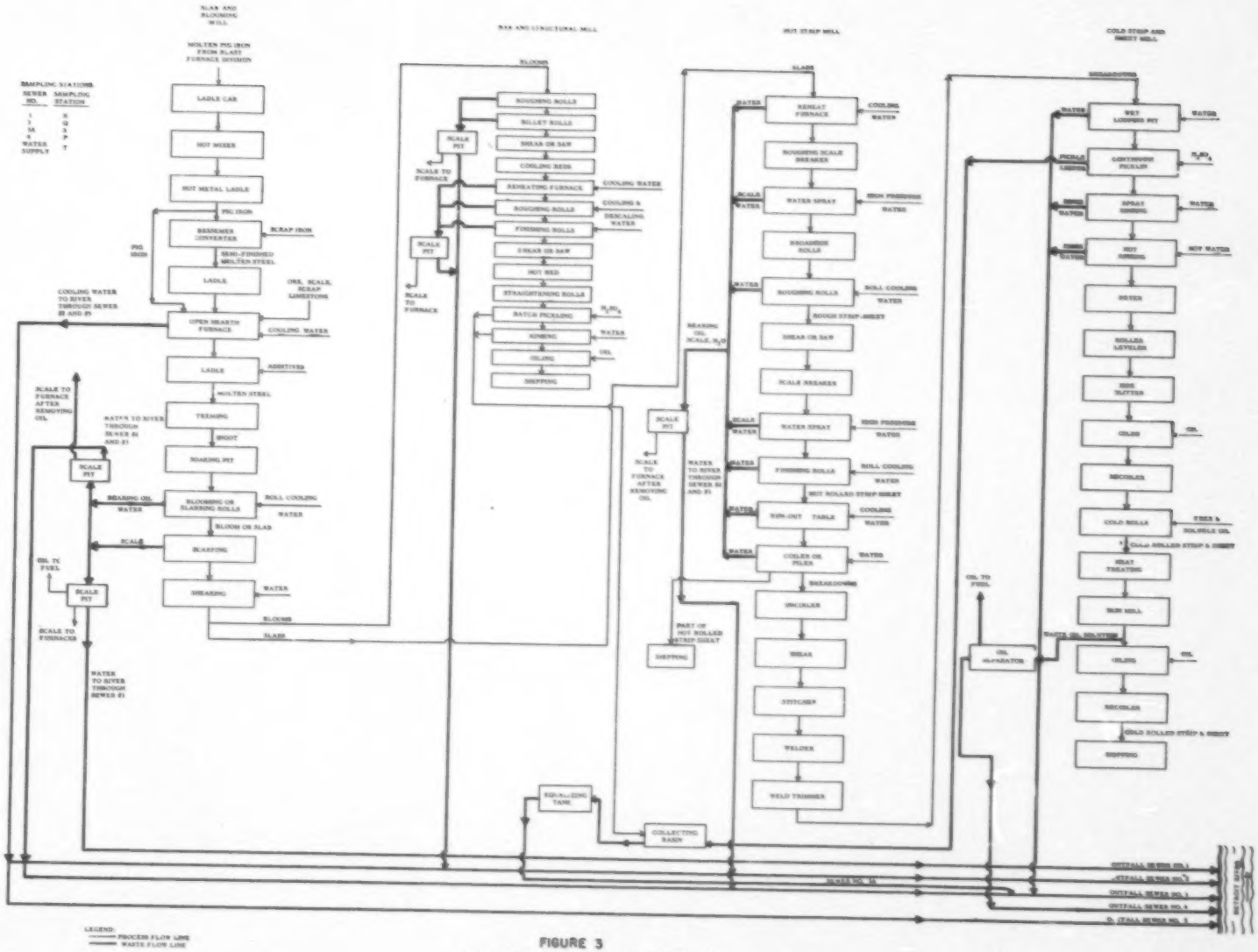


FIGURE 3

PROCESS FLOW DIAGRAM
SHOWING WASTE SOURCES
GREAT LAKES STEEL CORP.
ECORSE PLANT
ECORSE, MICHIGAN